

2.0 The K_d Model And Its Use In Contaminant Transport Modeling

2.1 Introduction

The concentration of contaminants in groundwater¹ is determined by the amount, concentration, and nature of contaminant present at the source, rate of release from the source, and a number of geochemical processes including aqueous and sorption geochemical processes (Section 2.2) and diffusion (Section 2.6). Recently, attention has been directed at additional geochemical processes that can enhance the transport of certain contaminants: colloid-facilitated transport of contaminants (Section 2.7) and anion exclusion (Section 2.8). These latter processes are difficult to quantify, and the extent to which they occur has not been determined. To predict contaminant transport through the subsurface accurately, it is essential that the important geochemical processes affecting the contaminant transport be identified and, perhaps more importantly, accurately described in a mathematically defensible manner. Dissolution/precipitation and adsorption/desorption are considered the most important processes affecting contaminant interaction with soils. Dissolution/precipitation is more likely to be the key process where chemical nonequilibrium exists, such as at a waste disposal facility (*i.e.*, point source), an area where high contaminant concentrations exist, or where steep pH or oxidation-reduction (redox) gradients exist. Adsorption/desorption will likely be the key process controlling contaminant migration in areas where chemical equilibrium exists, such as in areas far from the disposal facilities or spill sites.

The simplest and most common method of estimating contaminant retardation (*i.e.*, the inverse of the relative transport rate of a contaminant compared to that of water) is based on partition (or distribution) coefficient, K_d ,² values (Section 2.3.1). In turn, the K_d value is a direct measure of the partitioning of a contaminant between the solid and aqueous phases. It is an empirical metric that attempts to account for various chemical and physical retardation mechanisms that are influenced by a myriad of variables. Ideally, site-specific K_d values would be available for the range of aqueous and geological conditions in the system to be modeled.

Values for K_d not only vary greatly between contaminants, but also vary as a function of aqueous and solid phase chemistry (Delegard and Barney, 1983; Kaplan and Serne, 1995; Kaplan *et al.*, 1994c). For example, uranium K_d values can vary over 6 orders of magnitude depending on the composition of the aqueous and solid phase chemistry (see Volume II,

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For information regarding the background concentration levels of macro and trace constituents, including elements of regulatory-interest such as arsenic, cadmium, chromium, lead, and mercury, in soils and groundwater systems, the reader is referred to Lindsay (1979), Hem (1985), Sposito (1989, 1994), Langmuir (1997), and other similar sources and the references cited therein.

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A list of acronyms, abbreviations, symbols, and notation is given in Appendix A. A list of definitions is given in Appendix B.

Appendix J). A more robust approach to describing the partitioning of contaminants between the aqueous and solid phases is the parametric K_d model, which varies the K_d value according to the chemistry and mineralogy of the system at the node¹ being modeled (Section 2.3.2). Though this approach is more accurate, it has not been used frequently. The added complexity in solving the transport equation with the parametric K_d adsorption model and its empirical nature may be why this technique has been used sparingly.

Inherent in the K_d “linear isotherm” adsorption model is the assumption that adsorption of the contaminant of interest is independent of its concentration in the aqueous phase. Partitioning of a contaminant on soil can often be described using the K_d model, but typically only for low contaminant concentrations as would exist some distance away (far field) from the source of contamination. It is common knowledge that contaminant adsorption on soils can deviate from the linear relationship required by the K_d construct. This is possible for conditions as might exist in leachates or groundwaters near waste sources where contaminant concentrations are large enough to affect the saturation of surface adsorption sites. Non-linear isotherm models (Section 2.3.3) are used to describe the case where sorption relationships deviate from linearity.

Mechanistic models explicitly accommodate the dependency of K_d values on contaminant concentration, competing ion concentration, variable surface charge on the absorbent, and solution species distribution. Incorporating mechanistic or semi-mechanistic adsorption concepts into transport models is desirable because the models become more robust and, perhaps more importantly from the standpoint of regulators and the public, scientifically defensible. However, less attention will be directed to mechanistic adsorption models because the focus of this project is on the K_d model which is currently the most common method for quantifying chemical interactions of dissolved contaminants with soils for performance assessment, risk assessment, and remedial investigation calculations. The complexity of installing these mechanistic adsorption models into existing computer codes used to model contaminant transport is difficult to accomplish. Additionally, these models also require a more intense and costly data collection effort than will likely be available to many contaminant transport modelers, license requestors, or responsible parties. A brief description of the state of the science and references to excellent review articles are presented (Section 2.3.4).

The purpose of this chapter is to provide a primer to modelers and site managers on the key geochemical processes affecting contaminant transport through soils. Attention is directed at describing how geochemical processes are accounted for in transport models by using the partition coefficient (K_d) to describe the partitioning of aqueous phase constituents to a solid phase. Particular attention is directed at: (1) defining the application of the K_d parameter, (2) the explicit and implicit assumptions underlying its use in transport codes, and (3) the difference between the original thermodynamic K_d parameter derived from ion-exchange literature and its “empiricized” use in formulating the retardation factors used in contaminant

¹ A “node” is the center of a computation cell within a grid used to define the area or volume being modeled.

transport codes. In addition to geochemical processes, related issues pertaining to the effects of unsaturated conditions, chemical heterogeneity, diffusion, and subsurface mobile colloids on contaminant transport are also briefly discussed. These processes and their effects on contaminant mobility are summarized in a table at the end of this chapter.

2.2 *Aqueous Geochemical Processes*

Groundwater modelers are commonly provided with the total concentration of a number of dissolved substances in and around a contaminant plume. While total concentrations of these constituents indicate the extent of contamination, they give little insight into the forms in which the metals are present in the plume or their mobility and bioavailability. Contaminants can occur in a plume as soluble-free, soluble-complexed, adsorbed, organically complexed, precipitated, or coprecipitated species (Sposito, 1989). The geochemical processes that contribute to the formation of these species and their potential effect on contaminant transport are discussed in this chapter.

2.2.1 *Aqueous Complexation*

Sposito (1989) calculated that a typical soil solution will easily contain 100 to 200 different soluble species, many of them involving metal cations and organic ligands. A complex is said to form whenever a molecular unit, such as an ion, acts as a central group to attract and form a close association with other atoms or molecules. The aqueous species $\text{Th}(\text{OH})_4^\circ(\text{aq})$, $(\text{UO}_2)_3(\text{OH})_5^+$, and HCO_3^- are complexes with Th^{4+} (thorium), UO_2^{2+} (hexavalent uranium), and CO_3^{2-} (carbonate), respectively, acting as the central group. The associated ions, OH^- or H^+ , in these complexes are termed ligands. If 2 or more bonds are formed between a single ligand and a metal cation, the complex is termed a chelate. The complex formed between Al^{3+} and citric acid $[\text{Al}(\text{COO})_2\text{COH}(\text{CH}_2\text{COOH})]^+$, in which 2 COO^- groups and 1 COH group of the citric acid molecule are coordinated to Al^{3+} , is an example of a chelate. If the central group and ligands in a complex are in direct contact, the complex is called inner-sphere. If one or more water molecules is interposed between the central group and a ligand, the complex is outer-sphere. If the ligands in a complex are water molecules [e.g., as in $\text{Ca}(\text{H}_2\text{O})_6^{2+}$], the unit is called a solvation complex or, more frequently, a free species. Inner-sphere complexes usually are much more stable than outer-sphere complexes, because the latter cannot easily involve ionic or covalent bonding between the central group.

Most of the complexes likely to form in groundwater are metal-ligand complexes, which may be either inner-sphere or outer-sphere. As an example, consider the formation of a neutral sulfate complex with a bivalent metal cation (M^{2+}) as the central group:¹



¹ Unless otherwise noted, all species listed in equations in this appendix refer to aqueous species.

where the metal M can be cadmium, chromium, lead, mercury, strontium, *etc.* The equilibrium (or stability) constant, $K_{r,T}$, corresponding to Equation 2.1 is:

$$K_{r,T} = \frac{\{MSO_4^{\circ}(aq)\}}{\{M^{2+}\} \{SO_4^{2-}\}} \quad (2.2)$$

where quantities indicated by { } represent species activities. The equilibrium constant can describe the distribution of a given constituent among its possible chemical forms if complex formation and dissociation reactions are at equilibrium. The equilibrium constant is affected by a number of factors, including the ionic strength of the aqueous phase, presence of competing reactions, and temperature.

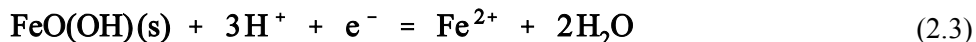
The most common complexing anions present in groundwater are HCO_3^-/CO_3^{2-} , Cl^- , SO_4^{2-} , and humic substances (*i.e.*, organic materials). Some synthetic organic ligands may also be present in groundwater at contaminated sites. Dissolved PO_4^{3-} can also be a strong inorganic complexant, but is generally not very soluble in natural groundwaters. The relative propensity of the inorganic ligands to form complexes with many metals is: $CO_3^{2-} > SO_4^{2-} > PO_4^{3-} > Cl^-$ (Stumm and Morgan, 1981). Carbonate complexation may be equally important in carbonate systems, especially for tetravalent metals (Kim, 1986; Rai *et al.*, 1990). There can be a large number of dissolved, small-chain humic substances present in groundwater and their complexation properties with metals and radionuclides are not well understood. Complexes with humic substances are likely to be very important in systems containing appreciable amounts of humic substances (>1 mg/l). In shallow aquifers, organic ligands from humic materials can be present in significant concentration and dominate the metal chemistry (Freeze and Cherry, 1979). The chelate anion, EDTA,¹ which is a common industrial reagent, forms strong complexes with many cations, much stronger than carbonate and humic substances (Kim, 1986). Some metal-organic ligand complexes can be fairly stable and require low pH conditions (or high pH for some metal-organic complexes) to dissociate the complex.

Complexation usually results in lowering the solution concentration (*i.e.*, activity) of the central molecule (*i.e.*, uncomplexed free species). Possible outcomes of lowering the activity of the free species of the metal include lowering the potential for adsorption and increasing its solubility, both of which can enhance migration potential. On the other hand, some complexants (*e.g.*, certain humic acids) readily bond to soils and thus retard the migration of the complexed metals.

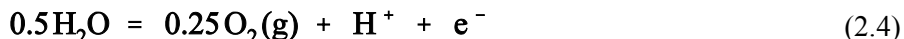
¹ EDTA is ethylene diamine triacetic acid.

2.2.2 Oxidation-Reduction (Redox) Chemistry

An oxidation-reduction (redox) reaction is a chemical reaction in which electrons are transferred completely from one species to another. The chemical species that loses electrons in this charge transfer process is described as oxidized, and the species receiving electrons is described as reduced. For example, in the reaction involving iron species:



the solid phase, goethite $[\text{FeO(OH)}(\text{s})]$, is the oxidized species, and Fe^{2+} is the reduced species. Equation 2.3 is a reduction half-reaction in which an electron in aqueous solution, denoted e^- , serves as one of the reactants. This species, like the proton in aqueous solution, is understood in a formal sense to participate in charge transfer processes. The overall redox reaction in a system must always be the combination of 2 half-reactions, an oxidation half-reaction and reduction half-reaction, such that the species e^- does not exist explicitly. For example, to represent the oxidation of Fe^{2+} , Equation 2.3 could be combined (or coupled) with the half-reaction involving the oxidation of H_2O :



Combining Equation 2.3 with Equation 2.4 results in the cancellation of the aqueous electron and the oxidation of Fe^{2+} via the reduction of $\text{O}_2(\text{g})$ and subsequent precipitation of hydrous iron oxide. This is a possible reaction describing Fe^{2+} leaching from a reduced environment in the near field to the oxidizing environment of the far field:



Equation 2.5 could represent a scenario in which Fe^{2+} is leached from a reducing environment, where it is mobile, into an oxidized environment, where Fe^{3+} precipitates as the mineral goethite.

The electron activity is a useful conceptual device for describing the redox status of aqueous systems, just as the aqueous proton activity is so useful for describing the acid-base status of soils. Similar to pH, the propensity of a system to be oxidized can be expressed by the negative common logarithm of the free-electron activity, pE:

$$\text{pE} = -\log \{\text{e}^-\} . \quad (2.6)$$

The range of pE in the natural environment varies between approximately 7 and 17 in the vadose zone (Sposito, 1989). If anoxic conditions exist, say in a bog area, then the pE may get as low as -3. The most important chemical elements affected by redox reactions in ambient groundwater are carbon, nitrogen, oxygen, sulfur, manganese, and iron. In contaminated groundwater, this list increases to include arsenic, cobalt, chromium, iodine, molybdenum, neptunium, plutonium, selenium, technetium, uranium, and others. Table 2.1 lists several redox-sensitive metals and the

Table 2.1. List of several redox-sensitive metals and their possible valence states in soil/groundwater systems.

Element	Valence States	Element	Valence States
Americium	+3, +4, +5, and +6	Neptunium	+3, +4, +5, and +6
Antimony	+3 and +5	Plutonium	+2, +3, +4, +5, and +6
Arsenic	+3 and +5	Ruthenium	+2, +3, +4, +6, and +7
Chromium	+2, +3, and +6	Selenium	-2, +4, and +6
Copper	+1 and +2	Technetium	+2, +3, +4, +5, +6, and +7
Iron	+2 and +3	Thallium	+1 and +3
Manganese	+2 and +3	Uranium	+3, +4, +5, and +6
Mercury	+1 and +2	Vanadium	+2, +3, +4, and +5

different valence states that they may be present as in soil/groundwater systems. The speciation of a metal in solution between its different valence states will depend on the site geochemistry, especially with respect to pH and redox conditions. Moreover, not all of the valence states for each metal are equally important from the standpoint of dominance in solution, adsorption behavior, solubility, and toxicity. For those redox-sensitive elements that are part of this project's scope (*i.e.*, chromium, plutonium, and uranium), these issues are discussed in detail in Volume II of this report.

There is a well defined sequence of reduction of inorganic elements (Table 2.2). When an oxidized system is reduced, the order that oxidized species disappear are O_2 , NO_3^- , Mn^{2+} , Fe^{2+} , HS^- , and H_2 . As the pE of the system drops below +11.0, enough electrons become available to reduce O_2 (g) to H_2O . Below a pE of 5, O_2 (g) is not stable in pH neutral systems. Above pE = 5, O_2 (g) is consumed in the respiration processes of aerobic microorganisms. As the pE decreases below 8, electrons become available to reduce NO_3^- to NO_2^- . As the system pE value drops into the range of 7 to 5, electrons become plentiful enough to support the reduction of iron and manganese in solid phases. Iron reduction does not occur until O_2 and NO_3^- are depleted, but manganese reduction can be initiated in the presence of NO_3^- . In the case of iron and manganese, decreasing pE results in solid-phase dissolution, because the stable forms of Mn(IV) and Fe(III) are solid phases. Besides the increase in solution concentrations of iron and manganese expected from this effect of lowered pE, a marked increase is usually observed in the aqueous phase concentrations of metals such as cadmium, chromium, or lead, and of ligands such as $H_2PO_4^-$ or

Table 2.2. Sequence of Principal Electron Acceptors in neutral pH aquatic systems (Sposito, 1989).

Reduction Half-Reactions	Range of Initial pE Values
$0.5 \text{ O}_2 (\text{g}) + 2 \text{ e}^- + 2 \text{ H}^+ = \text{H}_2\text{O}$	5.0 to 11.0
$\text{NO}_3^- + 2 \text{ e}^- + 2 \text{ H}^+ = \text{NO}_2^- + \text{H}_2\text{O}$	3.4 to 8.5
$\text{MnO}_2 (\text{s}) + 2 \text{ e}^- + 4 \text{ H}^+ = \text{Mn}^{2+} + 2 \text{ H}_2\text{O}$	3.4 to 6.8
$\text{FeOOH} (\text{s}) + \text{e}^- + 3 \text{ H}^+ = \text{Fe}^{2+} + 2 \text{ H}_2\text{O}$	1.7 to 5.0
$\text{SO}_4^{2-} + 8 \text{ e}^- + 9 \text{ H}^+ = \text{HS}^- + 4 \text{ H}_2\text{O}$	0 to -2.5
$\text{H}^+ + \text{e}^- = 0.5 \text{ H}_2 (\text{g})$	-2.5 to -3.7
$(\text{CN}_2\text{O})_n = n/2 \text{ CO}_2 (\text{g}) + n/2 \text{ CH}_4 (\text{g})$	-2.5 to -3.7

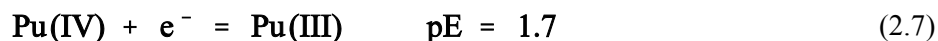
HMoO_4^- , accompanying reduction of iron and manganese. The principal cause of this secondary phenomenon is the desorption of metals and ligands that occurs when the adsorbents (*i.e.*, mostly iron and manganese oxides) to which they are bound become unstable and dissolve. Typically, the metals released in this fashion, including iron and manganese, are soon readsorbed by solids that are stable at low pE (*e.g.*, clay minerals or organic matter) and become exchangeable surface species.

These surface changes have an obvious influence on the availability (migration potential) of the chemical elements involved, particularly phosphorus. If a contaminant was involved in this dissolution/ exchange set of reactions, it would be expected that the contaminants would be less strongly associated with the solid phase.

As pE becomes negative, sulfur reduction can take place. If contaminant metals and radionuclides, such as Cr(VI), Pu (VI), or U(VI), are present in the aqueous phase at high enough concentrations, they can react with bisulfide (HS^-) to form metal sulfides that are quite insoluble. Thus, anoxic conditions can diminish significantly the solubility of some redox-sensitive contaminants.

Redox chemistry may also have a direct affect on contaminant chemistry. It can directly affect the oxidation state of several contaminants, including, arsenic, cobalt, chromium, iodine, molybdenum, neptunium, lead, plutonium, selenium, technetium, and uranium. A change in

oxidation in turn affects the potential of some contaminants to precipitate. For example, the reduction of Pu(IV),



makes plutonium appreciably less reactive in complexation [*i.e.*, Pu(III) stability constants are much less than those of Pu(IV)] and sorption/partitioning reactions (Kim, 1986). The reduction of U(VI) to U(III) or U(IV), has the opposite effect, *i.e.*, U(III) or U(IV) form stronger complexes and sorb more strongly to surfaces than U(VI). Reducing environments tend to make chromium, similar to uranium, less mobile, and arsenic more mobile.

Therefore, changes in redox may increase or decrease the tendency for reconcentration of contaminants, depending on the chemical composition of the aqueous phase and the contaminant in question. However, if the redox status is low enough to induce sulfide formation, reprecipitation of many metals and metal-like radionuclides can be expected. Redox-mediated reactions are incorporated into most geochemical codes and can be modeled conceptually. The resultant speciation distribution calculated by such a code is used to determine potential solubility controls and adsorption potential. Many redox reactions have been found to be kinetically slow in natural groundwater, and several elements may never reach redox equilibrium between their various oxidation states. Thus, it is more difficult to predict with accuracy the migration potential of redox-sensitive species.

2.2.3 Sorption

When a contaminant is associated with the solid phase, it is not known if it was adsorbed on to the surface of a solid, absorbed into the structure of a solid, precipitated as a 3-dimensional molecular structure on the surface of the solid, or partitioned into the organic matter (Sposito, 1989). Dissolution/precipitation and adsorption/desorption are considered the most important processes affecting metal and radionuclide interaction with soils and will be discussed at greater lengths than absorption and organic matter partitioning.

- Dissolution/precipitation is more likely to be the key process where chemical nonequilibrium exists, such as at a point source, an area where high contaminant concentrations exist, or where steep pH or redox gradients exist.
- Adsorption/desorption will likely be the key process controlling contaminant migration in areas where chemical equilibrium exists, such as in areas far from the point source.

A generic term devoid of mechanism and used to describe the partitioning of aqueous phase constituents to a solid phase is sorption. Sorption encompasses all of the above processes. It is frequently quantified by the partition coefficient, K_d , that will be discussed below (Section 2.3.1).

In many natural systems, the extent of sorption is controlled by the electrostatic surface charge of the mineral phase. Most soils have net negative charges. These surface charges originate from permanent and variable charges. The permanent charge results from the substitution of a lower valence cation for a higher valence cation in the mineral structure, where as the variable charge results from the presence of surface functional groups. Permanent charge is the dominant charge of 2:1 clays, such as biotite and montmorillonite. Permanent charge constitutes a majority of the charge in unweathered soils, such as exist in temperate zones in the United States, and it is not affected by solution pH. Permanent positive charge is essentially nonexistent in natural rock and soil systems. Variable charge is the dominant charge of aluminum, iron, and manganese oxide solids and organic matter. Soils dominated by variable charge surfaces are primarily located in semi-tropical regions, such as Florida, Georgia, and South Carolina, and tropical regions. The magnitude and polarity of the net surface charge changes with a number of factors, including pH. As the pH increases, the surface becomes increasingly more negatively charged. The pH where the surface has a zero net charge is referred to as the pH of zero-point-of-charge, pH_{zpc} (Table 2.3). At the pH of the majority of natural soils (pH 5.5 to 8.3), calcite, gibbsite, and goethite, if present, would be expected to have some, albeit little, positive charge and therefore some anion sorption capacity.

Table 2.3. pH of zero-point-of-charge, pH_{zpc} . [After Stumm and Morgan (1981) and Lehninger (1970)].

Material	pH_{zpc}
Gibbsite $[\text{Al}(\text{OH})_3]$	5.0
Hematite ($\alpha\text{-Fe}_2\text{O}_3$)	6.7
Goethite ($\alpha\text{-FeOOH}$)	7.8
Silica (SiO_2)	2
Feldspars	2 to 2.4
Kaolinite $[\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4]$	4.6
COOH	1.7 to 2.6 ¹
NH ₃	9.0 to 10.4 ¹
¹ These values represent the range of pK_a values for amino acids.	

2.2.3.1 Adsorption

Adsorption, as discussed in this report, is the net accumulation of matter at the interface between a solid phase and an aqueous-solution phase. It differs from precipitation because it does not include the development of a 3-dimensional molecular structure. The matter that accumulates in 2-dimensional molecular arrangements at the interface is the adsorbate. The solid surface on which it accumulates is the adsorbent.

Adsorption on clay particle surfaces can take place via 3 mechanisms. In the first mechanism, an inner-sphere surface complex is in direct contact with the adsorbent surface and lies within the Stern Layer (Figure 2.1). As a rule, the relative affinity of a contaminant to sorb will increase with its tendency to form inner-sphere surface complexes. The tendency for a cation to form an inner-sphere complex in turn increases with increasing valence (*i.e.*, more specifically, ionic potential¹) of a cation (Sposito, 1984).

The second mechanism creates an outer-sphere surface complex that has at least 1 water molecule between the cation and the adsorbent surface. If a solvated ion (*i.e.*, an ion with water molecules surrounding it) does not form a complex with a charged surface functional group but instead neutralizes surface charge only in a delocalized sense, the ion is said to be adsorbed in the diffuse-ion swarm, and these ions lie in a region called the diffuse sublayer (Figure 2.1). The diffuse-ion swarm and the outer-sphere surface complex mechanisms of adsorption involve exclusively ionic bonding, whereas inner-sphere complex mechanisms are likely to involve ionic, as well as covalent, bonding.

The mechanisms by which anions adsorb are inner-sphere surface complexation and diffuse-ion swarm association. Outer-sphere surface complexation of anions involves coordination to a protonated hydroxyl or amino group or to a surface metal cation (*e.g.*, water-bridging mechanisms) (Gu and Schulz, 1991). Almost always, the mechanism of this coordination is hydroxyl-ligand exchange (Sposito, 1984). In general, ligand exchange is favored at pH levels less than the zero-point-of-charge (Table 2.3). The anions CrO_4^{2-} , Cl^- , and NO_3^- , and to lesser extent HS^- , SO_4^{2-} , and HCO_3^- , are considered to adsorb mainly as diffuse-ion and outer-sphere-complex species.

¹ The ionic potential is the ratio of the valence to the ionic radius of an ion.

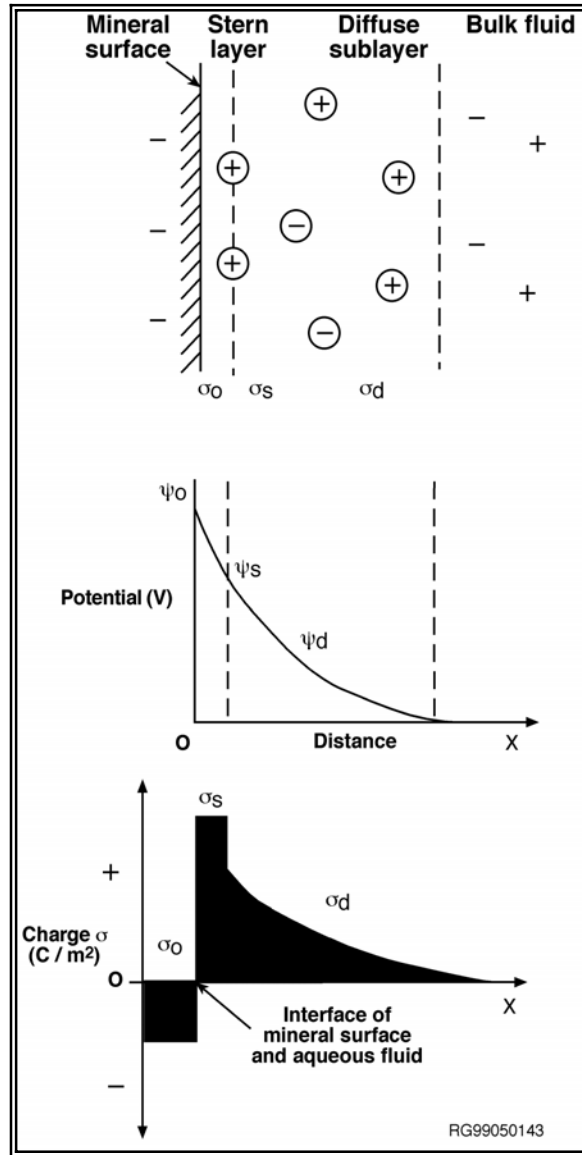
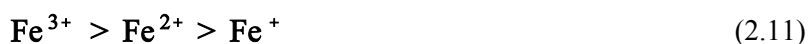
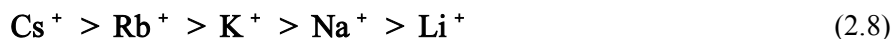


Figure 2.1. Diffuse double layer and surface charge of a mineral surface. (σ_0 , σ_s , and σ_d represent the surface charge at the surface, Stern layer, and diffuse layer, respectively; ψ_0 , ψ_s , and ψ_d represent the potential at the surface, Stern layer, and diffuse layer, respectively.)

As noted previously, the relative affinity of an adsorbent for a free-metal cation will generally increase with the tendency of a cation to form inner-sphere surface complexes, which in turn increases with higher ionic potential of a cation (Sposito, 1989). Based on these considerations and laboratory observations, the relative-adsorption affinity of metals has been described as follows (Sposito, 1989):



With respect to transition metal cations, however, ionic potential is not adequate as a single predictor of adsorption affinity, since electron configuration plays a very important role in the complexes of these cations. Their relative affinities tend to follow the Irving-Williams order:



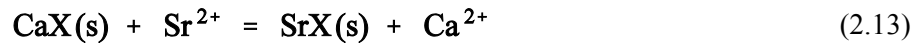
The molecular basis for this ordering is discussed in Cotton and Wilkinson (1972).

Adsorption of dissolved contaminants is very dependent on pH. As noted previously in the discussion of the pH of zero-point-of-charge, pH_{zpc} (Table 2.3), the magnitude and polarity of the net surface charge of a mineral changes with pH (Langmuir, 1997; Stumm and Morgan, 1981). At pH_{zpc} , the net charge of a surface changes from positive to negative. Mineral surfaces become increasingly more negatively charged as pH increases. At $\text{pH} < \text{pH}_{\text{zpc}}$, the surface becomes protonated, which results in a net positive charge and favors adsorption of contaminants present as dissolved anions. Because adsorption of anions is coupled with a release of OH^- ions, anion adsorption is greatest at low pH and decreases with increasing pH. At $\text{pH} > \text{pH}_{\text{zpc}}$, acidic dissociation of surface hydroxyl groups results in a net negative-charge which favors adsorption of contaminants present as dissolved cations. Because adsorption of cations is coupled with a release of H^+ ions, cation adsorption is greatest at high pH and decreases with decreasing pH. It should be noted that some contaminants may be present as dissolved cations or anions depending on geochemical conditions. In soil/groundwater systems containing dissolved carbonate, U(VI) may be present as dissolved cations (*e.g.*, UO_2^{2+}) at low to near-neutral pH values or as anions [*e.g.*, $\text{UO}_2(\text{CO}_3)_3^{4-}$] at near neutral to high pH values. The adsorption of U(VI) on iron oxide minerals (Waite *et al.*, 1994) is essentially 0 percent at pH values less than approximately 3, increases rapidly to 100 percent in the pH range from 5 to 8, and rapidly decreases to 0 percent at pH values greater than 9. This adsorption behavior for U(VI) (see Volume II) is reflected in the K_d values reported in the literature for U(VI) at various pH values.

It should also be noted that the adsorption of contaminants to soil may be totally to partially reversible. As the concentration of a dissolved contaminant declines in groundwater in response to some change in geochemistry, such as pH, some of the adsorbed contaminant will be desorbed and released to the groundwater.

2.2.3.1.1 Ion Exchange

One of the most common adsorption reactions in soils is ion exchange. In its most general meaning, an ion-exchange reaction involves the replacement of 1 ionic species on a solid phase by another ionic species taken from an aqueous solution in contact with the solid. As such, a previously sorbed ion of weaker affinity is exchanged by the soil for an ion in aqueous solution. Most metals in aqueous solution occur as charged ions and thus metal species adsorb primarily in response to electrostatic attraction. In the cation-exchange reaction:



Sr^{2+} replaces Ca^{2+} from the exchange site, X. The equilibrium constant (K_{ex}) for this exchange reaction is defined by the equation:

$$K_{\text{ex}} = \frac{\{\text{SrX(s)}\} \{\text{Ca}^{2+}\}}{\{\text{CaX(s)}\} \{\text{Sr}^{2+}\}} \quad (2.14)$$

There are numerous ion-exchange models and they are described by Sposito (1984) and Stumm and Morgan (1981). The original usage of K_d , often referred to as the thermodynamic K_d , is a special case of Equation 2.14. When one of the cations, such as Sr as the ^{90}Sr contaminant, is present at trace concentrations, the amount of Ca on the exchange sites CaX(s) remains essentially constant, as does Ca^{2+} in solution. These two terms in Equation 2.14 can thus be replaced by a constant and

$$K_d = \frac{\{\text{SrX(s)}\}}{\{\text{Sr}^{2+}\}} \quad (2.15)$$

The ranges of cation exchange capacity (CEC, in milliequivalents/100 g) exhibited by several clay minerals are listed in Table 2.4 based on values tabulated in Grim (1968).

2.2.3.2 Precipitation

The precipitation reaction of dissolved species is a special case of the complexation reaction in which the complex formed by 2 or more aqueous species is a solid. Precipitation is particularly important to the behavior of heavy metals (e.g., nickel and lead) in soil/groundwater systems. As an example, consider the formation of a sulfide precipitate with a bivalent radionuclide cation (M^{2+}):



Table 2.4. Cation exchange capacities (CEC) for several clay minerals (Grim, 1968).

Mineral	CEC (milliequivalents/100 g)
Chlorite	10 - 40
Halloysite · 2H ₂ O	5 - 10
Halloysite · 4H ₂ O	40 - 50
Illite	10 - 40
Kaolinite	3 - 15
Sepiolite-Attapulgite-Palygorskite	3 - 15
Smectite	80 - 150
Vermiculite	100 - 150

The equilibrium constant, $K_{r,T}$, corresponding to Equation 2.16 is:

$$K_{r,T} = \frac{\{M(HS)_2(s)\}}{\{M^{2+}\} \{HS^-\}^2} = \frac{1}{\{M^{2+}\} \{HS^-\}^2} \quad (2.17)$$

By convention, the activity of a pure solid phase is set equal to unity (Stumm and Morgan, 1981). The solubility product, $K_{sp,T}$, corresponding to dissolution form of Equation 2.16 is thus:

$$K_{sp,T} = \{M^{2+}\} \{HS^-\}^2 . \quad (2.18)$$

Precipitation of radionuclides is not likely to be a dominant reaction in far-field (*i.e.*, a distance away from a point source) or non-point source plumes because the contaminant concentrations are not likely to be high enough to push the equilibrium towards the right side of Equation 2.16. Precipitation or coprecipitation is more likely to occur in the near field as a result of high salt concentrations in the leachate and large pH or pE gradients in the environment. Coprecipitation is the simultaneous precipitation of a chemical element with other elements by any mechanism (Sposito, 1984). The 3 broad types of coprecipitation are inclusion, absorption, and solid solution formation.

Solubility-controlled models assume that a known solid is present or rapidly forms and controls the solution concentration in the aqueous phase of the constituents being released. Solubility

models are thermodynamic equilibrium models and typically do not consider the time (*i.e.*, kinetics) required to dissolve or completely precipitate. When identification of the likely controlling solid is difficult or when kinetic constraints are suspected, empirical solubility experiments are often performed to gather data that can be used to generate an empirical solubility release model.¹ A solubility limit is not a constant value in a chemically dynamic system. That is, the solubility limit is determined by the product of the thermodynamic activities of species that constitute the solid (see Equation 2.18). If the system chemistry changes, especially in terms of pH and/or redox state, then the individual species activities likely change. For example, if the controlling solid for plutonium is the hydrous oxide $\text{Pu}(\text{OH})_4$, the solubility product, K_{sp} , (as in Equation 2.18) is the plutonium activity multiplied by the hydroxide activity taken to the fourth power, *i.e.*, $\{\text{Pu}\} \{\text{OH}\}^4 = \text{solubility product}$. The solubility product is fixed, but the value of $\{\text{Pu}\}$ and $\{\text{OH}\}$ can vary. In fact, if the pH decreases 1 unit ($\{\text{OH}\}$ decreases by 10), then for K_{sp} to remain constant, $\{\text{Pu}\}$ must increase by 10^4 , all else held constant. A true solubility model must consider the total system and does not reduce to a fixed value for the concentration of a constituent under all conditions. Numerous constant concentration (*i.e.*, empirical solubility) models are used in performance assessment activities that assume a controlling solid and fix the chemistry of all constituents to derive a fixed value for the concentration of specific contaminants. The value obtained is only valid for the specific conditions assumed.

When the front of a contaminant plume comes in contact with uncontaminated groundwater, the system enters into nonequilibrium conditions. These conditions may result in the formation of insoluble precipitates which are best modeled using the thermodynamic construct, K_{sp} (*i.e.*, the solubility product described in Equation 2.18). Precipitation is especially common in groundwater systems where the pH sharply increases. Additionally, soluble polymeric hydroxo solids of metallic cations tend to form as the pH increases above 5 (Morel and Hering, 1993). At pH values greater than 10, many transition metals and transuranic hydroxide species become increasingly more soluble. The increase in solubility results from the formation of anionic species, such as $\text{Fe}(\text{OH})_4^-$, $\text{UO}_2(\text{CO}_3)_2^{2-}$, or $\text{UO}_2(\text{CO}_3)_3^{4-}$. A demonstration calculation of the solubility of U(VI) as a function of pH is given in Chapter 5. As the pH of the plume decreases from values greater than 11 to ambient levels below approximately pH 8, some metal hydroxo solids, such as $\text{NpO}_2(\text{s})$ and $\text{Fe}(\text{OH})_3(\text{s})$, may precipitate. The solubility behaviors of the contaminants included in the first phase of this project are discussed in detail in the geochemistry background sections in Volume II of this report.

¹ An empirical solubility release model is a model that is mathematically similar to solubility, but has no identified thermodynamically acceptable controlling solid.

2.3 Sorption Models

2.3.1 Constant Partition Coefficient (K_d) Model

The constant partition coefficient, K_d , is a measure of sorption and is defined as the ratio of the quantity of the adsorbate (*i.e.*, metal or radionuclide) adsorbed per unit mass of solid to the quantity of the adsorbate remaining in solution at equilibrium. For the reaction



the mass action expression for K_d (typically in units of ml/g) is

$$K_d = \frac{A_i}{C_i} \quad (2.20)$$

where A = free or unoccupied surface adsorption sites,
 C_i = total dissolved adsorbate remaining in solution at equilibrium ($\mu\text{g/ml}$), and
 A_i = adsorbate on the solid at equilibrium ($\mu\text{g/g}$).

Describing the K_d in terms of this simple reaction assumes that A is in great excess with respect to C_i and that the activity of A_i is equal to 1. The K_d term is valid only for a particular adsorbent and applies only to those aqueous chemical conditions (*e.g.*, adsorbate concentration, solution/electrolyte matrix, temperature) in which it was measured. Also inherent in the K_d term are the assumptions that the system is reversible and is independent of the adsorbate concentration in the aqueous phase.

Essentially all of the assumptions associated with the thermodynamically defined K_d value (Equation 2.20) are violated in the common protocols used to measure K_d values for use in contaminant transport codes. Typically, the K_d for a given adsorbent is determined in the laboratory using soil from the study area and actual or simulated groundwater to which an adsorbate is added at some trace concentration. The values of C_i and A_i are operationally defined as the adsorbate concentrations measured in the fractions that passed through or were retained by, respectively, filtration by some known filter pore size, such as 0.45- μm diameter. An important practical limitation of the measurement of K_d values is that the total concentration or radioactivity of the adsorbate is measured, thereby treating the adsorbate as a single species. This assumption is not an inherent requirement, but it is generally applied for convenience. A hypothetical example of the species measured in a neptunium K_d experiment are presented in Equation 2.21:

$$= \frac{\sum_{n=1}^{\infty} \{ \text{NpO}_2\text{X(s)} \} + \{ \text{NpO}_2\text{Y(s)} \} + \{ \text{NaNpO}_2(\text{CO}_3)(\text{s}) \} + \{ \text{Na}_3\text{NpO}_2(\text{CO}_3)_2(\text{s}) \} +}{\sum_{n=1}^{\infty} \{ \text{NpO}_2^+ \} + \{ \text{NpO}_2(\text{OH})_2^+ \} + \{ \text{NpO}_2(\text{OH})^\circ(\text{aq}) \} + \{ \text{NpO}_2(\text{CO}_3)_2^{2-} \} + \dots} \quad (2.21)$$

where { } indicate activity, and X and Y are 2 different mineral species. The solid phase in this example contains 4 solid neptunium species, including the species adsorbed to species X and Y and the species precipitated as $\text{NaNpO}_2(\text{CO}_3)$ and $\text{Na}_3\text{NpO}_2(\text{CO}_3)_2$. The dissolved phase in this example contains 4 neptunium species including NpO_2^+ , $\text{NpO}_2(\text{OH})_2^-$, $\text{NpO}_2(\text{OH})^\circ (\text{aq})$, and $\text{NpO}_2(\text{CO}_3)_2^{2-}$. Using common laboratory techniques, experimentalist would not be able to measure the concentrations of each of these dissolved and solid phases. Consequently, the experimentalist can not distinguish between adsorbed and precipitated species. In this example, there are more than just 1 dissolved and sorbed species, thereby violating an important assumption underlying the K_d value. Furthermore, many solutes have been observed to sorb more readily than desorb from mineral or organic surfaces, a phenomena referred to as hysteresis.

In chemistry, the term conditional K_d is often used (Jenne, 1977) to identify experimentally derived partition coefficients that may not necessarily denote an equilibrium value or require some of the other assumptions inherent in the more rigorous use of the K_d term. The definition of conditional K_d is given in Equation 2.22:

$$\text{Conditional } K_d = \frac{\sum_{n=1}^{\infty} A_i}{\sum_{n=1}^{\infty} C_i} \quad (2.22)$$

where A_i = sorbed species
 C_i = dissolved species.

Compared to Equation 2.20, Equation 2.22 more clearly represents the example represented by Equation 2.21. No attempt will be made in this text to distinguish between the true thermodynamic and the conditional K_d .

An important limitation of the constant K_d model is that it does not address sensitivity to changing conditions. If the groundwater properties (*e.g.*, pH and solution ionic strength) change, a different K_d value should be used in the model. This limitation will be discussed further in Section 2.2.3.2.

Chemical retardation, R_f , is defined as,

$$R_f = \frac{v_p}{v_c}, \quad (2.23)$$

where v_p = velocity of the water through a control volume
 v_c = velocity of contaminant through a control volume.

The chemical retardation term does not equal unity when the solute interacts with the soil; almost always the retardation term is greater than 1 due to solute sorption to soils. In rare cases, the retardation factor is actually less than 1, and such circumstances are thought to be caused by anion exclusion (Section 2.8). To predict the effects of retardation, sorption processes must be described in quantitative terms. The K_d provides such a quantitative estimate. Knowledge of the K_d and of media bulk density and porosity for porous flow, or of media fracture surface area, fracture opening width, and matrix diffusion attributes for fracture flow, allows calculation of the retardation factor. For porous flow with saturated moisture conditions, the R_f is defined as

$$R_f = 1 + \frac{\rho_b}{n_e} K_d \quad (2.24)$$

where ρ_b = porous media bulk density (mass/length³)
 n_e = effective porosity of the media at saturation.

For 1-dimensional advection-dispersion flow with chemical retardation, the transport equation can be written as

$$\frac{\partial C_i}{\partial t} = \frac{\left[D_x \frac{\partial^2 C_i}{\partial x^2} - v_x \frac{\partial C_i}{\partial x} \right]}{R_f(i)} \quad (2.25)$$

where C_i = concentration of contaminant species I in solution (mass/length³),
 D_x = dispersion coefficient of species I (length²/time),
 v_x = pore velocity of groundwater (length/time), and
 $R_f(i)$ = retardation factor for species i.

For simplicity, radioactive decay has been omitted from Equation 2.25.

When the K_d term is incorporated into the retardation factor, R_f , as in Equation 2.24, the R_f term is also devoid of sorption mechanism, *i.e.*, adsorption, absorption, or precipitation can not be distinguished from one another as the mechanism by which the contaminants partitioned to the solid phase. Furthermore, incorporating the K_d term into the R_f term assumes implicitly that the reactions go to equilibrium and are reversible and that the chemical environment along the solute flow path does not vary in either space or time (Muller *et al.*, 1983). Although these assumptions rarely hold true in the natural environment, single-value model parameters are generally employed, with the justification that the approach builds conservatism into the analysis. Additionally, the paucity of geochemical data at most sites precludes a more rigorous conceptual model (Section 2.3.3).

2.3.2 Parametric K_d Model

Clearly, the greatest limitation of using K_d values to calculate retardation terms (Equation 2.24) is that it describes solute partitioning between the aqueous and solid phases for only 1 set of environmental conditions. Such homogeneity does not exist in nature and therefore greatly compromises the usefulness of the constant. For example, when the aqueous phase chemistry was varied, americium K_d values in a Hanford sediment ranged from 0.2 to 53 ml/g, roughly a 200-fold range (Delegard and Barney, 1983). Additional variability in the americium K_d values, albeit less, were observed when slightly different Hanford sediments were used: 4.0 to 28.6 ml/g (Delegard and Barney, 1983: Solution 1). Using similar aqueous phases but diverse soils, Sheppard *et al.* (1976) measured americium K_d values ranging from 125 to 43,500 ml/g.

Another practical conceptual model for adsorption is called the parametric K_d model. The K_d value in this model varies as a function of empirically derived relationships with aqueous and solid phase independent parameters. Thus, it has the distinct advantage of being more robust and removes the burden of determining new K_d values for each environmental condition. Because the value of a K_d term is a function of a large number of variables, it is common to systematically vary several parameters simultaneously in 1 experimental study. Factorial design strategies are most often invoked to determine the systematic change resulting from varying the independent variables on the dependent variables, typically the partition coefficient (Box and Behnken, 1960; Cochran and Cox, 1957; Davies, 1954; Plackett and Burman, 1946). Statistical methods commonly used to derive quantitative predictor equations include standard linear or nonlinear regression (Snedecor and Cochran, 1967), stepwise regression (Hollander and Wolfe, 1973), and adaptive-learning networks (Mucciardi *et al.*, 1979, 1980). All these techniques have been used to develop empirical relationships describing K_d values in terms of other variables (Routson and Serne, 1972; Serne *et al.*, 1973; Routson *et al.*, 1981; Delegard and Barney, 1983).

The empirical predictor equations commonly take the form of a nonlinear polynomial expression. For example, after evaluating solutions consisting of several sodium salts, organic chelates, and acids, Delegard and Barney (1983) derived with the following expression for an americium K_d value:

$$\text{Log } K_d (\text{Americium}) = 2.0 + 0.1 [\text{NaOH}] - 26.8 [\text{HEDTA}] + 153.4 [\text{HEDTA}]^2 \quad (2.26)$$

Numerous salts were found to have no significant effect on americium K_d values and therefore were not included in the expression. Delegard and Barney (1983) also evaluated higher exponential and logarithmic terms and determined that these terms did not improve the predictive capabilities of the expression (*i.e.*, the regression coefficients were not significant at $P \leq 0.05$).

It is critical that parametric K_d equations, such as Equation 2.26, be used to calculate K_d values for systems only within the range of the independent variables used to create the equation. In the case of Equation 2.26, the range of independent variables used to generate the model were selected to simulate a plume emanating from a steel-lined concrete tank that contained strong

caustic and high sodium contents. Using Equation 2.26 to generate americium K_d values for a plume low in pH and sodium concentrations would not be appropriate.

These types of statistical relationships are devoid of causality and therefore provide no certain information on the mechanism by which the radionuclide partitioned to the solid phase, whether it be by adsorption, absorption, or precipitation. For example, the statistical analyses may suggest a very strong relationship between pH and the K_d term, when the actual sorption process may be controlled by iron oxide adsorption. Because pH and the surface charge of iron oxides are covariants, a statistical relationship could be calculated, suggesting that sorption is solely caused by pH.

The parametric K_d model can be used in the retardation factor term (Equation 2.24) and the transport equation (Equation 2.25). When used in the transport equation, the code must also keep track of the current value of the independent variables (*e.g.*, [NaOH] and [HEDTA]¹ for the examples described in Equation 2.26) at each point in space and time to continually update the concentration of the independent variables affecting the K_d value. Thus, the code must track many more parameters, and some numerical solving techniques (*e.g.*, closed-form analytical solutions) can no longer be used to perform the integration necessary to solve for contaminant concentration. Generally, computer codes that can accommodate the parametric K_d model use a chemical subroutine to update the K_d value used to determine the R_f , when called by the main transport code. The added complexity in solving the transport equation with the parametric K_d sorption model and its empirical nature may be the reasons this approach has been used sparingly.

2.3.3 Isotherm Adsorption Models

Some adsorption studies are conducted in a systematic fashion to evaluate the effects of various parameters on K_d . The results of a suite of experiments evaluating the effect of contaminant concentration on adsorption, while other parameters are held constant, are called an “adsorption isotherm.” For soils, it is common knowledge that contaminant adsorption can deviate from the linear relationship required by the K_d construct discussed in Section 2.3.1. If it was possible to keep increasing the amount of contaminant in solution contacting soil, all adsorption sites would become saturated at some contaminant concentration and the linear relationship between contaminant adsorbed to contaminant in solution would no longer hold. Isotherm models are used to describe the case where sorption relationships deviate from linearity. For many short-lived radionuclides, the mass present never reaches quantities large enough to start loading surface adsorption sites to the point that the linear K_d relationship is not accurate. However, long-lived radionuclides and stable elements, such as RCRA-regulated metals, can be found in leachates and groundwaters near waste sources at concentrations large enough to affect the saturation of surface adsorption sites.

¹ HEDTA is N-(2-hydroxyethyl) ethylenediaminetetraacetic acid.

In situations where the amount of contaminant loaded on the available adsorption sites is large enough to impact the linear adsorption construct, isotherm models are often invoked. Three adsorption isotherm models used frequently are the Langmuir, Freundlich, and Dubinin-Radushkevich models.

The Langmuir model was originally proposed to describe adsorption of gas molecules onto homogeneous solid surfaces (crystalline materials) that exhibit one type of adsorption site (Langmuir, 1918). Many investigators have tacitly extended the Langmuir adsorption model to describe adsorption of solution species onto solid adsorbents including heterogeneous solids such as soils. The Langmuir model for adsorption is

$$A_i = \frac{K_L A_m C_i}{1 + K_L C_i} \quad (2.27)$$

where A_i = amount of adsorbate adsorbed per unit mass of solid
 K_L = Langmuir adsorption constant related to the energy of adsorption
 A_m = maximum adsorption capacity of the solid
 C_i = equilibrium solution concentration of the adsorbate.

Substituting $1/B$ for K_L , one obtains

$$A_i = \frac{A_m C_i}{B + C_i} \quad (2.28)$$

A plot of values for A_i (y-axis) versus values of C_i (x-axis) passes through the origin and is nearly linear at low values of C_i . As C_i increases, A_i should approach A_m . Taking the reciprocal of Equation 2.28 and multiplying both sides of the equation by $A_i A_m$ yields

$$A_i = -B \frac{A_i}{C_i} + A_m . \quad (2.29)$$

Then, by plotting A_i on the y-axis and (A_i/C_i) on the x-axis, one can determine the value of $-B$ from the slope of the best fit line and the value of A_m from the intercept. Sposito (1984) and Salter *et al.* (1981a) cite several instances where the Langmuir isotherm has successfully fit trace adsorption by natural substrates. Further Sposito (1984) and Salter *et al.* (1981b) discuss modifications of the Langmuir model to accommodate 2 distinct sites and competition of 2 adsorbates (the nuclide and the ion it replaces on the adsorbent) which further extend this conceptual model's usefulness on natural substrates. In the parlance of Giles *et al.* (1974) [also see Sposito (1984)], the Langmuir adsorption isotherm is the L-curve. For L-curve isotherms, the initial slope of A_i (amount of solute adsorbed per unit mass of solid) [plotted on the y-axis] versus C_i (equilibrium solution concentration of the adsorbate) [plotted on the x-axis] is large, but the slope decreases as C_i increases. This forms the concave shaped curve shown in Figure 2.2. The various curves depicted in Figure 2.2 are discussed in greater detail later in this section.

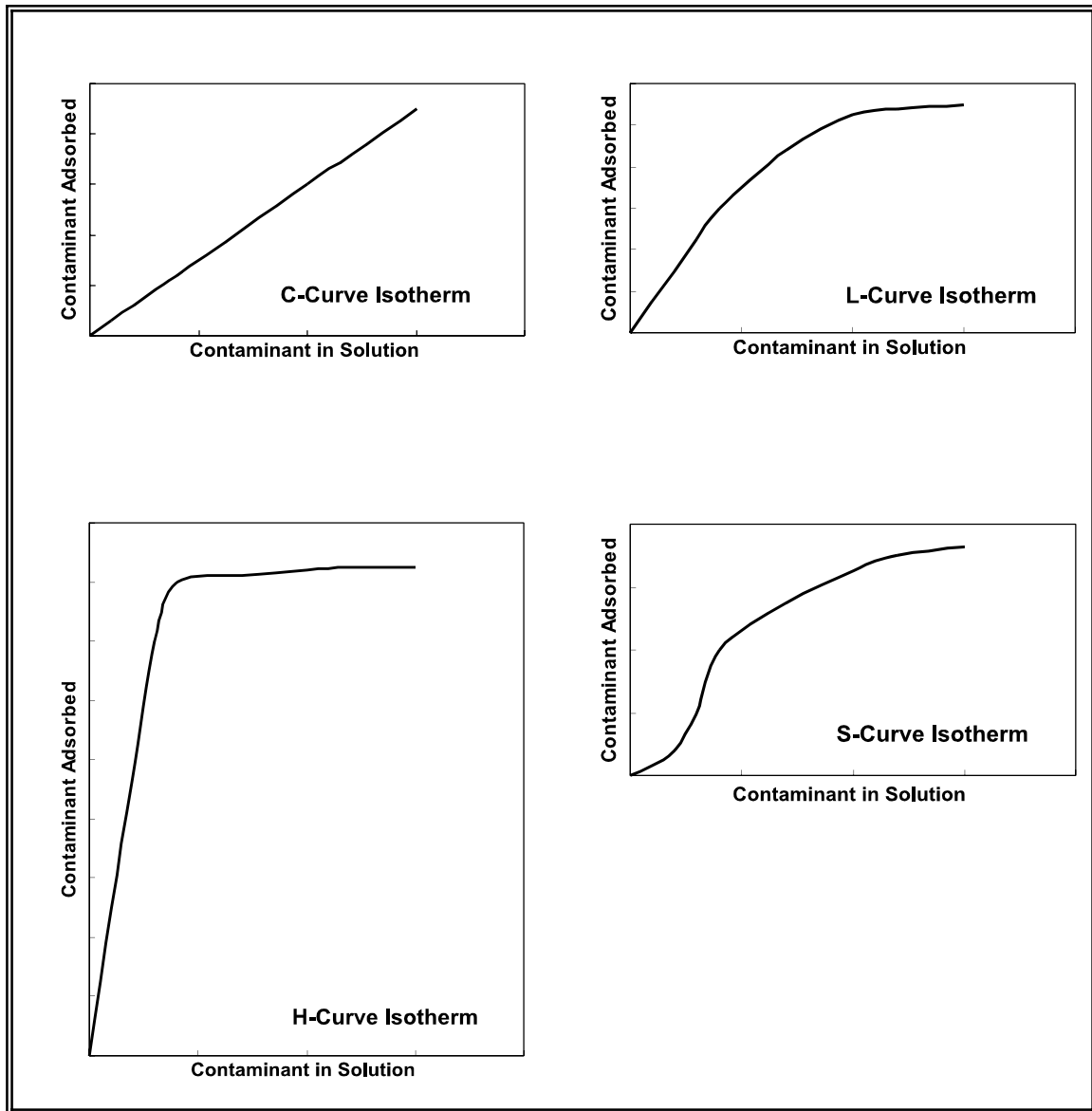


Figure 2.2. Four types of adsorption isotherm curves shown schematically in parlance of Giles *et al.* (1974).

The Freundlich isotherm model (Freundlich, 1926) is defined as:

$$A_i = K_F C_i^N \quad (2.30)$$

where A_i = amount of adsorbate adsorbed per unit mass of solid
 C_i = equilibrium solution concentration of the adsorbate
 K_F = Freundlich adsorption constant
 N = constant.

The Freundlich equation is sometimes written with the exponent in Equation 2.30 being $1/N$ instead of N . The Freundlich model does not account for finite adsorption capacity at high concentrations of solute, but when considering trace constituent adsorption, ignoring such physical constraints is usually not critical. The Freundlich isotherm can be transformed to a linear equation by taking the logarithms of both sides of Equation 2.30:

$$\log A_i = \log K_F + N \log C_i \quad (2.31)$$

When $\log A_i$ is plotted on the y-axis and $\log C_i$ on the x-axis, the best-fit straight line has a slope of N , and $\log K_F$ is its intercept. When $N=1$, the Freundlich isotherm, represented by Equation 2.31 reduces to a linear relationship. Because A_i/C_i is the ratio of the amount of solute adsorbed to the equilibrium solution concentration (the definition of K_d), the Freundlich K_F is equivalent to the value of K_d .

Because adsorption isotherms at very low solute concentrations are often linear, either the Freundlich isotherm with N equaling 1 or the Langmuir isotherm with $K_L \cdot C_i$ much greater than 1 fits the data. The value of N for the adsorption of many radionuclides is often significantly different from 1, such that nonlinear isotherms are observed. In such cases, the Freundlich model is a better predictor than the Langmuir model. Sposito (1984) shows how the Freundlich isotherm is equivalent to the Langmuir isotherm where the parameter K_F is log normally distributed. Sposito (1984) also stresses that the Freundlich isotherm only applies to data obtained at low values of C_i (concentration of contaminant in the equilibrium solution).

A third adsorption model that has been used recently in nuclide studies is the Dubinin-Radushkevich isotherm (Dubinin and Radushkevich, 1947). This model is applicable for the adsorption of trace constituents. Should the adsorbent surface become saturated or the solute exceed its solubility product, the model is inappropriate. The Dubinin-Radushkevich model is more general than the Langmuir model, because it does not require either homogeneous adsorption sites or constant adsorption potential. Its mathematical form is

$$A_i = A_m e^{-K_{DR} \epsilon^2} \quad (2.32)$$

where A_i = observed amount of adsorbate adsorbed per unit mass
 A_m = sorption capacity of adsorbent per unit mass
 K_{DR} = Dubinin-Radushkevich adsorption constant

$$\begin{aligned}
\epsilon &= RT \ln (1 + 1/C_i) \\
R &= \text{gas constant} \\
T &= \text{temperature (in Kelvin)} \\
C_i &= \text{equilibrium solution concentration of the adsorbate.}
\end{aligned}$$

The Dubinin-Radushkevich equation can be transformed to

$$\ln A_i = \ln A_m - K_{DR} \epsilon^2 \quad (2.33)$$

A plot of $\ln A_i$ (y-axis) versus ϵ^2 (x-axis) allows the estimation of $\ln A_m$ as the intercept and $-K_{DR}$ as the slope of the resultant straight line. Ames *et al.* (1982) successfully used this model to describe adsorption of uranium and cesium onto basalt and its weathering products.

All 3 isotherm models can be compared against data from experiments that systematically vary the mass of a trace constituent or radionuclide while holding all other parameters as constant as possible. It is important to consider the total mass of the element present, including all stable and other radioactive isotopes, when evaluating isotherms. It is incorrect to calculate isotherms based on only one isotope if the system includes several (both stable and radioactive) for a particular element. For convenience, isotherm experiments tend to consider only the total concentration or radioactivity content and thus lumps all species for a given isotope.

It can be argued that all 3 isotherm models are based on physicochemical processes or mechanisms. If the experiments are performed and characterized rigorously to assure equilibrium conditions and constancy of variables aside from the trace constituent concentration, then the resultant isotherm constants undoubtedly have some relationship to adsorption capacities and to site adsorption energies. On the other hand, any suite of experiments that can be plotted as amount adsorbed versus amount in solution at the time of measurement can also be analyzed using these models to see whether predictive equations can be determined. The latter empirical approach is a step up in sophistication over the constant K_d model.

Giles *et al.* (1974) state that isotherm shapes are largely determined by the adsorption mechanism, and thus can be used to explain the nature of adsorption. The S-curve (Figure 2.2) is explained by Giles *et al.* (1974) as adsorption where the presence of the individual solute molecules bound to the solid interact with each other. This increases the strength of the individual solute bonds to the solid surface when the solid has low contaminant loading. Thus, for a brief period during adsorption, the first bound molecules enhance adsorption of the next molecules that bind to the solid. The slope of the isotherm increases from the lowest concentration of contaminant where surface coverage is so sparse that adsorbed molecules cannot interact. At some point, the sites become laden with contaminant and the slope of the adsorption isotherm starts decreasing again. Sposito (1984) gives another plausible explanation for the S-curve, wherein complexing solution ligands compete with the surface sites for the contaminant until the complexing ligands are complexed with the contaminant and additional contaminant is free to adsorb with less or no complexant competition.

The L-curve (Figure 2.2) is the classical Langmuir curve where the loading of contaminant on the solid starts to decrease the adsorption slope as sites become saturated. The adsorption of many RCRA-regulated metals and long-lived radionuclides on soils have been successfully described by Langmuir isotherms. Giles *et al.* (1974) shows that the L-shaped curve is found for systems where the activation energy for the adsorption/desorption of each adsorbate is unaffected by the other adsorbates and solvent (water) in the systems. Rai and Zachara (1984) include one compilation of Langmuir isotherms for RCRA-regulated metals.

The H-curve (Figure 2.2) is an extreme version of the L-curve isotherm. The H-curve describes adsorption of “high-affinity” adsorbates onto solid adsorbents. The activation energy of the desorption of the analyte of interest is much larger than other species in the solution.

The C-curve (constant slope) (Figure 2.2) suggests that the number of available sorption sites remains constant throughout the whole range of solute concentrations (whereas the K_d model applies to low solute concentrations) or the available surface expands proportionally with the amount of material adsorbed up to the point where all adsorption sites are filled. Giles *et al.* (1974) discuss two conceptual models on how the available sorption sites can expand in proportion to the adsorbed mass. The model where the adsorbent is microporous and the adsorbate has a much higher affinity for the adsorbent surfaces than the water is most germane for soils. The adsorbates enter the microporous solid and act like a molecular wedge to open up more sorption sites through continued penetration.

It is difficult to assess whether one should put much weight on isotherm shape constructs discussed by Giles *et al.* (1974) as a vehicle to elaborate on adsorption mechanisms. The number of discrete crystalline minerals and amorphous phases and coatings present in soils as well as the multitude of inorganic and organic ligands found or expected in soil solutions combine to make a quantitative description of contaminant adsorption and the controlling mechanisms a formidable activity. To quote Sposito (1984, pg. 122), “The adherence of experimental sorption data to an adsorption isotherm provides no evidence as to the actual mechanism of the sorption process in soils and sediments.” We value this statement and suggest that isotherms are just one step more sophisticated than the constant K_d construct in delineating or quantifying adsorption of contaminants.

It must be stressed that isotherm models, as expressed by Equations 2.27, 2.30, and 2.32, explicitly consider dependency of the partition coefficient on only the solution concentration of the contaminant of interest. Isotherm models do not consider dependence on other solid and solution parameters that can influence adsorption, such as those discussed in Volume II for each contaminant of interest.

The incorporation of adsorption isotherm models into transport codes is relatively easy. Each of the aforementioned isotherm equations can be rearranged to calculate a partition coefficient, K_d , that is a function of C , the solution concentration of the radionuclide, and 1 or 2 constants. As the transport model solves for C , substitution of an equation that depends only upon C (and derivable constants) for the K_d in the retardation factor (see Equations 2.23 and 2.24) should be

straightforward. For simple cases, analytical closed-formed solutions are possible, or numerous numerical approximation schemes can be used. Thus, with little additional work or increases in computer storage requirements, most transport codes can be formulated to predict radionuclide migration with an adsorption isotherm model. It should be repeated, however, that this approach accounts for the dependency of K_d on only one parameter, the concentration of the radionuclide. If the mass of contaminant in the environment is low, and complicating factors such as complexing agents and type S sorption behavior are not expected, all 3 adsorption isotherms discussed above are readily simplified to the constant K_d model.

2.3.4 Mechanistic Adsorption Models

Mechanistic models explicitly accommodate for the dependency of K_d values on contaminant concentration, competing ion concentration, variable surface charge on the adsorbent, and solute species solution distribution. Incorporating mechanistic, or semi-mechanistic, adsorption concepts into transport models is attempted because the models become more robust and, perhaps more importantly from the standpoint of regulators and the public, scientifically defensible. However, less attention will be directed to these adsorption models because we judge them of little practical use for the majority of site-screening applications. The complexity of installing these mechanistic adsorption models into existing transport codes is difficult to accomplish. Additionally, mechanistic adsorption models also require a more intense and costly data collection effort than will likely be available to the majority of EPA, DOE, and NRC contaminant transport modelers and site remediation managers. A brief description of the state of the science is presented below. References to excellent review articles have been included in the discussion to provide the interested reader with additional information.

Experimental data on interactions at the mineral-electrolyte interface can be represented mathematically through 2 different approaches: (1) empirical models and (2) mechanistic models. An empirical model can be defined as a mathematical description of the experimental data without any particular theoretical basis. For example, the K_d , Freundlich isotherm, Langmuir isotherm, Langmuir Two-Surface Isotherm, and Competitive Langmuir construct are considered empirical models by this definition (Sposito, 1984). Mechanistic models refer to models based on thermodynamic concepts such as reactions described by mass action laws and material balance equations. Four of the most commonly used mechanistic models include the Helmholtz, Gouy-Chapman, Stern, and Triple Layer models (Sposito, 1984). The empirical models are often mathematically simpler than mechanistic models and are suitable for characterizing sets of experimental data with a few adjustable parameters, or for interpolating between data points. On the other hand, mechanistic models contribute to an understanding of the chemistry at the interface and are often useful for describing data from complex multicomponent systems for which the mathematical formulation (*i.e.*, functional relationships) for an empirical model might not be obvious. Mechanistic models can also be used for interpolation and characterization of data sets in terms of a few adjustable parameters (Westall, 1986). However, it is important to realize that adjustable parameters are required for both mechanistic and empirical models, except the K_d model. The need to include adjustable parameters in order to apply/solve mechanistic models compromises their universal application.

Any complete mechanistic description of chemical reactions at the mineral-electrolyte interface must include a description of the electrical double layer (Figure 2.1). While this fact has been recognized for years, a satisfactory description of the double layer at the mineral-electrolyte interface still does not exist. Most electrical double layer models were written for specific conditions and are only accurate under limited environmental conditions. For instance, the Stern model is a better model for describing adsorption of inner-sphere complexes, whereas the Gouy-Chapman model is a better model for describing outer-sphere or diffuse swarm adsorption (Sposito, 1984; Westall, 1986) (Figure 2.1).

Truly mechanistic models are rarely, if ever, applied to complex natural soils (Schindler and Sposito, 1991; Sposito, 1984; Westall and Hohl, 1980; Westall, 1986; Westall, 1994). The primary reason for this is because the surfaces of natural mineral are very irregular and difficult to characterize. These surfaces consist of different microcrystalline structures and/or coatings of amorphous phases that exhibit quite different and complex chemical properties when exposed to solutions. Thus, examination of the surface by virtually any experimental method yields only averaged characteristics of the surface and the interface. Parsons (1982) discussed the surface chemistry of single crystals of pure metals and showed that the potential of zero charge of different crystal faces of the same pure metal can differ by over 400 mV. For an oxide surface, this difference was calculated by Westall (1986) to be energetically equivalent to a variation in the pH of zero-point-of-charge (pH_{zpc}) of more than 6 pH units. This example indicated that an observable macroscopic property of a polycrystalline surface might be the result of a combination of widely different microscopic properties and that characterizations of these surfaces will remain somewhat operational in nature.

Another fundamental problem encountered in characterizing reactions at the mineral-electrolyte interface is the coupling between electrostatic and chemical interactions, which makes it difficult to distinguish the effects of one from the effects of the other. Westall and Hohl (1980) have shown that many models for reactions at the mineral-electrolyte interface are indeterminate in this regard.

2.4 Effects of Unsaturated Conditions on Transport

The major pathway for contaminant transport in arid areas is through unsaturated soils. Although considerable effort has been expended over the past few years to quantify the mobility of contaminants and determine factors that influence contaminant mobility, little work has been done to investigate the transport of radionuclides under conditions of partial saturation.

At unsaturated moisture conditions, the pores are partially filled with air and water. The water in the pores is partly held in place by attractive forces of capillarity. A key hydrologic measurement in unsaturated (vadose zone) soils is the soil-water matric potential (or suction). Matric potential is defined as, the amount of work that must be done per unit of soil solution in order to transport, reversibly and isothermally, an infinitesimal quantity of water from a pool of soil solution at a given elevation above the water table (and at atmospheric pressure) to the soil pores at the same elevation and pressure (SSSA, 1997). When the work (or energy) is expressed

on a weight basis, the matric potential is expressed in units of length (*i.e.*, m or cm). Matric potential is always negative (*i.e.*, energy is gained in going from a saturated solution to unsaturated soil pores, because of adsorptive forces and capillarity of porous material). Matric suction is the absolute value of matric potential and is used for convenience to express the matric forces (potentials) as positive values. By definition, at the water table, both the matric potential and matric suction are zero.

Unsaturated flow properties include the unsaturated hydraulic conductivity and the water retention characteristics (relationship between water content and matric suction values). Analogous to saturated flow where the advective flux¹ is the product of the saturated hydraulic conductivity and the gradient of the hydrostatic head,² the advective flow in unsaturated sediments is the product of the unsaturated conductivity and the matric potential (or suction) gradient. The suction gradient defines the direction of flow (from areas of low to high suction). At most vadose zone sites there have been no direct measurements of either the unsaturated conductivity or water retention characteristics for sediments. Generally only water contents have been measured (often by neutron logging) in boreholes or from split-spoon samples.

When the soil is saturated, nearly all pores are filled and hydraulic conductivity is at a maximum. As the soil becomes unsaturated, some of the pores become air-filled and the conductive cross-sectional areas are decreased. In addition, the first pores to empty are the largest and most conductive and tortuosity is increased for any water molecule that is still actively advecting through the porous media (*i.e.*, the water must find less direct pathways around these empty pores). In unsorted soils, the large pores that resulted in high conductivity at saturation become barriers to liquid flow between smaller pores during unsaturated flow. Hence, the transition from saturated to unsaturated flow may result in a steep drop in hydraulic conductivity of several orders of magnitude as the tension increase from 0 to 1 bar. At higher tensions (*i.e.*, more unsaturation), conductivity may be so low that steep pressure gradients are required for any appreciable soil water flow to occur. An interesting corollary of the pore size-conductivity relationship is that at, or near, saturation, a sandy soil conducts water more rapidly than a clay soil with many micropores. When the soils are unsaturated, however, many of the micropores in the clay soil remain filled, and consequently, the hydraulic conductivity in the clay soil does not decrease nearly as sharply as it does in sandy soil under the same tension. If the soil water does not move, then the contaminant in, or contacted by, the soil water does not move except by diffusion (Section 2.6), which is a relatively slow process (Rancon, 1973).

In modeling contaminant transport in unsaturated conditions, Equation 2.24 takes the form:

$$R_f = 1 + \frac{\rho_b}{\theta} K_d \quad (2.34)$$

¹ The flux density is the volume of water flowing through a cross-section area per unit time.

² The hydraulic gradient is the head drop per unit distance in the flow direction.

where θ , the volumetric water content of the soil (cm^3 water/ cm^3 total), replaces n (cm^3 void space/ cm^3 total), soil porosity, in Equation 2.24. Equation 2.27 explicitly assumes that the extent to which contaminants sorb to soils, the K_d value, is constant as a function of the volumetric water content. This relationship is convenient for modeling; however, its validity is not certain. There have been experiments to test this assumption, and the results have been mixed (Gee and Campbell, 1980; Knoll, 1960; Lindenmeier *et al.*, 1995; Nielsen and Biggar, 1961; Nielsen and Biggar, 1962; Routson and Serne, 1972).

There are theoretical reasons for believing that K_d values vary as a function of volumetric water content. First, as the soil becomes increasingly unsaturated there will be a smaller percentage of the total exchange sites in contact with the aqueous phase. For example, if only half of the exchange sites of a soil come into contact with the aqueous phase, then the effective exchange capacity of the soil is only half of that, had all the available exchange sites come into contact with the aqueous phase. Therefore, as less mineral surface is exposed to the aqueous phase, the lower the effective exchange capacity becomes because less of the surface is exposed to the solute of interest. On the other hand, the clay fraction of the soil constitutes the largest exchange capacity and smallest pore sizes. Because the smaller pores are involved in unsaturated flow, there may be little measurable effect on the exchange capacity of the soil in unsaturated conditions. Another reason for believing that K_d values would vary with degree of saturation is because in the unsaturated systems the aqueous phase is in closer contact with the soil surfaces. Solutes in the middle of large pores have less interaction with soil surfaces than solutes nearer to the soil surfaces. In unsaturated conditions, the middle of large pores tend to be empty, resulting in a greater percentage of pore water being in close contact with the soil surface. Finally, the ionic strength of the aqueous phase tends to increase closer to the clay surfaces. Thus, as a soil dehydrates, the system tends to have a higher ionic strength. The K_d value for many cations tends to decrease with increases in ionic strength.

The average size of individual pores is larger for coarse- versus fine-textured soils, despite the finer-grained soils having a larger total porosity. In saturated soil, all of the pore space is water-filled; the pores are continuous or “connected,” and generally water conducting. As a saturated soil is desaturated, the larger pores drain first, and air becomes a barrier to water flow. Water flow in unsaturated soils may occur as film flow along the particle surface, or as “matrix flow” through smaller, water-filled pores. The unsaturated flow regime is expected to differ in unsaturated coarse- versus fine-textured soils, with film flow dominating the former, and matrix flow the latter. This conceptualizations is illustrated in Figure 2.3. Recent improvements in imaging technologies [*i.e.*, magnetic resonance imaging (MRI) and X-ray microtomography] have increased our ability to directly distinguish the distribution of water, such as films at the particle surface, pendular water forming a meniscus at the intersection of two particles, and water held in small pores. Improved imaging of the water distribution in unsaturated soils is increasing fundamental understanding of the unsaturated flow regime.

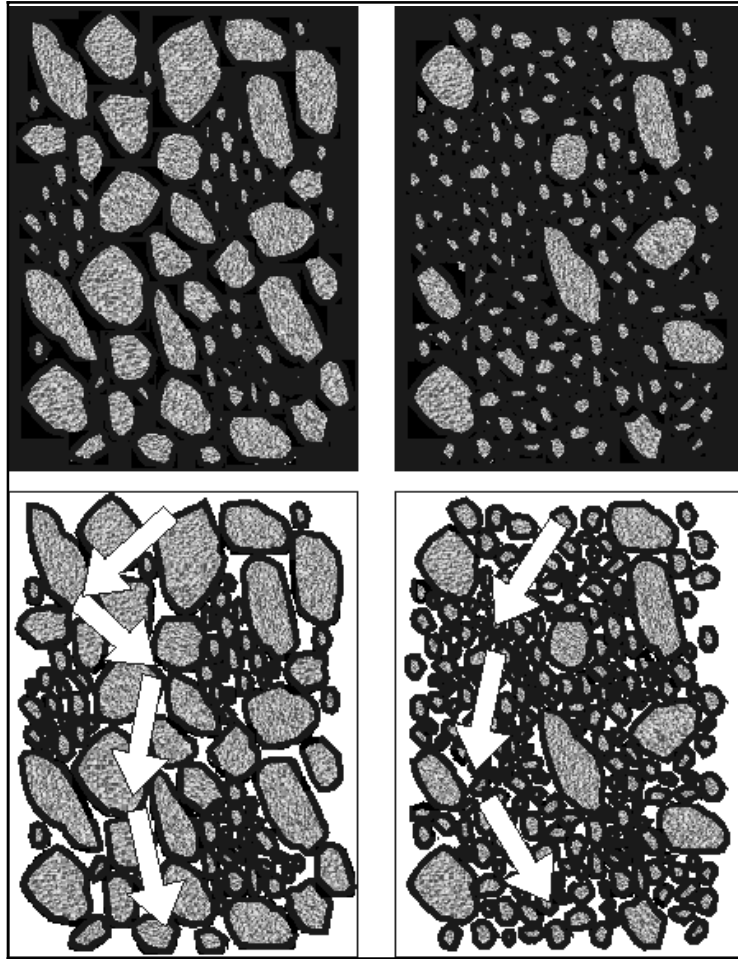


Figure 2.3. Schematic diagram for conceptual model of water distribution in saturated (top two figures) and unsaturated soils (bottom two figures) suggesting differences in the unsaturated flow regime (indicated by arrows) for soils with varying texture. [The two figures on left represent coarse-textured soils, whereas the two figures on the right represent fine-textured soils. Soil particles, air, and water are shown, respectively, in stippled gray, white, and black.]

As a soil is progressively desaturated, retained water is held with increasingly greater “suction,” expressed as the matric or negative pressure potential. Hydraulic conductivity, K_h (m/sec) reflects the ease of water flow through the media and decreases with decreasing moisture saturation (*i.e.*, greater resistance to flow at lower water contents). Hydraulic conductivity is also highly dependent on soil texture. Relationships between hydraulic conductivity, matric potential, and water content are well-established (Hillel, 1998; Jury *et al.*, 1991). The spatial variability of hydraulic conductivity and the effect on solute transport in saturated soils have been the subject of modeling investigations (*e.g.*, Dagan, 1984; Gelhar and Axness, 1983; Tompson and Gelhar, 1990). Various modeling approaches are reviewed by Koltermann and Gorelick (1996) and compared to field data by Sudicky (1986). For unsaturated soils, research has focussed on scaling, and the effect of spatially variable hydraulic conductivity on water flow, infiltration, and drainage (Hopmans *et al.*, 1988; Nielsen *et al.*, 1973; Peck *et al.*, 1977; Warrick and Amoozegar-Fard, 1979).

In unsaturated soils, the pathway for water flow can become more tortuous, and water held in films and in small pores can be “disconnected” with respect to the flow regime. In reviewing water flow and transport in the vadose zone, Nielsen *et al.* (1986) noted that in addition to water held within aggregates, immobile water may exist in thin liquid films around soil particles, in dead-end pores, or as relatively isolated regions associated with unsaturated flow. Immobile water is also apparent in saturated systems. Most investigations that consider mass transfer between mobile and immobile water regions have been conducted in saturated systems.

Immobile water is manifest as hydraulic heterogeneity, and is typically characterized with a “dual porosity” or “two-region” model (Coats and Smith, 1964; Haggerty and Gorelick, 1995; van Genuchten and Wierenga, 1976). The liquid phase is partitioned into mobile and immobile (stagnant or micro-porosity) regions, where advective solute transport is limited to the mobile water phase. The mobile water fraction, ϕ_m , is defined as the volume fraction of water associated with the mobile domain, θ_m , relative to the total water content, θ_v (*i.e.*, $\phi_m = \theta_m/\theta_v$). Transport in and out of the immobile water domain is diffusion-limited. A small degree of hydraulic heterogeneity can be characterized by increased hydrodynamic dispersion (Pickens *et al.*, 1981).

However, a 2-region flow regime is required as the fraction of stagnant water increases. The importance of particle scale properties (Ball *et al.*, 1990), specifically mass transfer between mobile and immobile water regions (Haggerty and Gorelick, 1995), in affecting larger-scale transport has been noted. Compared to the standard advection-dispersion model with sorption, physical models accounting for mobile-immobile water described better reactive solute transport in a field-scale natural gradient tracer study (Goltz and Roberts, 1986), although other factors contributing to non-ideal behavior may also be important (Brusseau, 1994).

The development of heterogeneous unsaturated flow, in non-aggregated porous media was suggested in several studies comparing the transport of non-sorptive tracers at various degrees of moisture saturation (Biggar and Nielsen, 1962; Bond and Wierenga, 1990; Nielsen and Biggar, 1961). The fraction of immobile water increased from 4 to 40 percent when water content was decreased from 71 to 55 percent moisture saturation in a disturbed sand column (Gaudet *et al.*,

1977). It is important to note one study with contrasting results where a decrease in dispersion (heterogeneity) was observed when moisture content was reduced from 100 to 97 and 93 percent (Jardine *et al.*, 1993). This was observed in undisturbed cores and the effect was attributed to the elimination of macropore flow for the slightly unsaturated conditions. Changes in hydraulic heterogeneity at lower water contents were not evaluated.

Recent studies of unsaturated sands (Gamerding *et al.*, 1998, Gamerding and Kaplan, 1999) confirmed the findings of Gaudet *et al.* (1977). The development of an increasing fraction of immobile water (*i.e.*, decreasing ϕ_m) is illustrated in Figure 2.4 for sandy soils (filled diamond and square symbols). Data for a fine-textured soil (loamy fine sand, represented by the filled triangle in Figure 2.4) with a high ϕ_m is consistent with the conceptual model (above) that water held in the smaller pores of unsaturated fine-texture soils remains conductive.

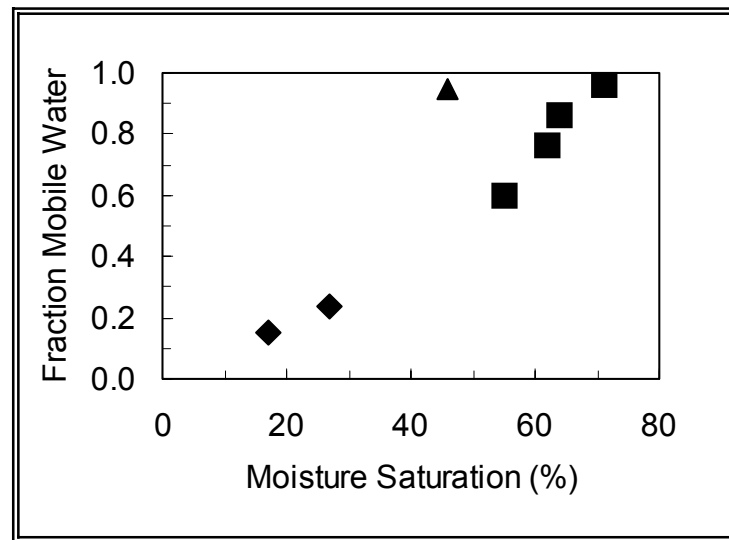


Figure 2.4. Development of hydraulic heterogeneity (decreasing ϕ_m) in unsaturated, non-aggregated soils with decreasing moisture saturation. [Filled diamond and square symbols represent data for sandy soils from Gamerding and Kaplan (1999) and Gaudet *et al.* (1977), respectively. The filled triangle symbol is data for finer-textured loamy fine sand from Bond and Wierenga (1990).]

The unsaturated flow regime is expected to differ in soils dominated by coarse-textured particles in contrast to those with fine-textured particles. As shown schematically in Figure 2.3, the flow regime will consist of film flow along the surfaces of large particles, versus matrix flow through small pores formed by fine particles. Hydraulic conductivity varies with soil texture and decreases with decreasing moisture saturation. Hydraulic heterogeneity resulting from a 2-region, mobile-immobile water, flow domain, increases in unsaturated soils. Limited data suggest a dependence on soil texture for non-aggregated soils where the heterogeneity is not apparent for saturated conditions.

In summary, the development of hydraulic heterogeneity in non-aggregated unsaturated soils has long been identified. However, the implications for the sorptive and transport behavior of contaminants are unknown. Current transport models account for lower, and spatially variable, hydraulic conductivity in unsaturated soils. Hydraulic heterogeneity resulting from mobile-immobile water domains has been considered when modeling transport in saturated systems. Fewer investigations have considered unsaturated systems.

2.5 Effects of Chemical Heterogeneity on Transport

In context of contaminant adsorption and transport, chemical heterogeneity refers in this report to the variability in particle surface reactivity. Iron oxide minerals are abundant in the subsurface environment and mineral coatings consisting of Fe(III)-oxides can be a significant source of reactivity for contaminant adsorption in a variety of soil systems [*e.g.*, Smith and Jenne (1991) as summarized by Thompson *et al.* (1996)]. The effect of chemical heterogeneity arising from spatially variable Fe(III)-oxide abundance has been considered in modeling the transport of cobalt (Brusseau and Zachara, 1993) and reactive transport of uranyl-citrate (Thompson *et al.*, 1996) and Co-EDTA (Szecsody *et al.*, 1998a, 1998b) complexes. Modeling studies of reactive solute transport in saturated systems have shown that chemical heterogeneities result in non-ideal transport behavior (Bosma *et al.*, 1993, Sugita *et al.*, 1995).

Different approaches for representing chemical heterogeneity (*i.e.*, spatial distribution of sorption sites) have been considered when combining processes in reactive flow and transport models for saturated systems (Szecsody *et al.*, 1998a, 1998b; Thompson *et al.*, 1996). The effect of a homogeneous versus a heterogeneous (spatially variable) distribution of reactive sites was compared in simulations of reactivity in batch (non-flowing) and column systems (Szecsody *et al.*, 1998b). While reactive site heterogeneity had a small effect in batch systems, it was highly significant in columns. A major conclusion was that particle-scale heterogeneities significantly influenced the interactions of sorptive (and reactive) solutes during advective flow (Szecsody *et al.*, 1998b).

2.5.1 Coupled Hydraulic and Chemical Heterogeneity

The absence of well-controlled laboratory investigations of contaminant transport in physically and chemically heterogeneous porous media has been noted (Brusseau and Zachara, 1993). The increased importance of particle scale heterogeneity in flowing versus non-flowing systems has

implications for the advance from saturated to unsaturated solute transport. Variability in accessibility to reactive sites by mobile solutes is expected to increase with increased tortuosity. Predictive models that incorporate heterogeneity usually focus on reactive site abundance (Szecsody *et al.*, 1998a; Thompson *et al.*, 1996), although the length of Fe(III)-oxide inclusions has been considered (Szecsody *et al.*, 1998a). In an unsaturated soil, the distribution and abundance of reactive sites is considered to be the same as when the soil is saturated. However, the observed increase in hydraulic heterogeneity with decreased moisture saturation suggests greater variability in access to reactive sites, and thus an even greater significance of particle scale chemical heterogeneity during transport in unsaturated soils. Models which consider spatially variable reaction capacity and accessibility have been developed for saturated porous media flow (Reichle *et al.*, 1998).

Unsaturated systems have received less attention, with few investigations considering the combined effects of hydraulic and chemical heterogeneity. Russo (1989a,b) evaluated spatially variable hydraulic conductivity from a different perspective, considering the effect of solution properties on soil properties which included hydraulic conductivity and water content. The spatial variability of pesticide transport and sorption in unsaturated soil was evaluated in field, laboratory column, and batch experiments (Elabd *et al.*, 1986; Jury *et al.*, 1986). Although average K_d values from batch and column experiments were similar, there was no correlation between values measured in batch (non-flowing) and column systems (Jury *et al.*, 1986). For 18 of the 36 samples, retardation in laboratory columns with undisturbed field cores was greater than predicted from the batch K_d value (Elabd *et al.*, 1986). Non-sorptive tracer (*e.g.*, chloride) transport did not show the same degree of heterogeneity as the pesticides, suggesting sorption variability in addition to flow heterogeneity (Jury *et al.*, 1986). This research indicates that sorption during unsaturated transport is not accurately predicted from measurements in batch systems.

An important issue for modeling transport in a chemically heterogeneous system is the correlation between reactivity and other parameters that are used to characterize the medium. Correlations between reactivity and permeability (or hydraulic conductivity) are often used, but the appropriate form of the correlation for specific systems can be debated (Tompson *et al.*, 1996). Data to support specific correlations between particle size and particle surface reactivity are sparse. Consequently, approximate negative correlations are often used (Burr *et al.*, 1994; Tompson, 1993; Tompson *et al.*, 1996), or alternative possibilities of negative, positive, or no correlation are evaluated (Bosma *et al.*, 1993, 1996; Tompson, 1993;).

Experimental evidence for a negative correlation between particle size and the sorption of organic chemicals has been demonstrated (Barber *et al.*, 1992; Karickhoff *et al.*, 1979; Schwarzenbach and Westall, 1981). However, the findings of Ball *et al.* (1990) for the Canadian Forces Base Borden Aquifer soils do not support this trend. A significant, but weak, correlation between strontium sorption and " $\ln K_h$ " was observed for the Borden Aquifer soils (Robin *et al.*, 1991). Preferential sorption of strontium to the fine-textured soil fraction and with micaceous minerals of the coarsest fraction of Chalk River aquifer soils from Ontario, Canada was observed by Pickens *et al.* (1981).

The importance of grain scale properties in determining the sorption and transport of reactive solutes and the need for systematic study of factors that affect correlation for specific porous media and reactions is evident. Due to the increasing complexity of unsaturated systems, the success of simply extending relationships that are developed in saturated systems is questionable. Fundamental research in unsaturated systems with measurement of relevant parameters relating media properties to chemical heterogeneity and reactive transport is needed.

In summary, the relationships between soil texture, porosity, moisture saturation, hydraulic heterogeneity and sorption are complex. Hydraulic heterogeneity in unsaturated soils results from disconnectivity of pore water which can be caused by thin liquid films around soil particles, dead-end pores, or relatively isolated regions associated with unsaturated flow. The proportion of disconnected or immobile water increases with decreasing moisture saturation (Figure 2.4). The unsaturated flow regime is thought to depend on the soil texture, where film flow is more likely to dominate in unsaturated coarse-textured soils, and matrix flow through small pores prevailing in fine-textured soils.

2.6 Diffusion

The transport of matter in the absence of bulk flow is referred to as diffusion. The flux of matter due to diffusion is proportional to the concentration gradient and is a molecular process. In general terms, the flux, J_{ix} , of component I in the x direction is

$$J_{ix} = -D \frac{dC_i}{dx} \quad (2.35)$$

where D = proportionality constant or diffusion coefficient with the dimensions of length²/time

C_i = concentration of constituent i.

The J_{ix} has the dimensions of moles/length²/time, and the negative sign indicates that flow of constituent I in the x direction is also in the direction of lower I concentration. In an infinitely dilute aqueous solution, the movement is quantified by the diffusion coefficient, D . For most simple aqueous species, D is about 10^{-9} m²/s or 10^{-5} cm²/s.

Atkinson (1983), Atkinson *et al.* (1986), and Atkinson and Nickerson (1988) present a useful conceptual model for describing the transport of contaminants through a porous media such as soil. The authors consider that the transport is a combination of both physical processes, such as diffusion, and chemical processes, such as precipitation/solubility and adsorption/desorption. In the constrained geometry of a porous media, such as soil, the D is reduced compared to the D in free aqueous solution. The D for a species within a porous media is defined as D_p and is equal to

$$D_p = \frac{D \delta}{\tau^2} \quad (2.36)$$

where δ = constrictivity of the porous media
 τ = tortuosity of the porous media.

For experimentalists, it is convenient to measure the average flux of a contaminant per unit area of the porous media in relation to the concentration gradient of the contaminant in the aqueous phase. The concentration gradient in the aqueous phase is influenced by the volume fraction of the void space in the porous media (the porosity, n_e). This leads to another equation that defines the "intrinsic" diffusion coefficient, D_i :

$$D_i = D_p n_e = \frac{D n_e \delta}{\tau^2} \quad (2.37)$$

A key assumption herein is that all the porosity in the porous media is interconnected and thus can contribute to diffusion of the contaminant. All three parameters, porosity (n_e), constrictivity (δ), and tortuosity (τ), characterize the physical contribution to diffusion through the porous media.

The chemical contributions to diffusion can potentially be quite varied, such as ion exchange, specific adsorption, precipitation, and lattice substitution. If a very simple chemical process is assumed, reversible surface adsorption having fast kinetics and a linear isotherm (*i.e.*, K_d), then diffusion of a reactive contaminant can be characterized by an apparent diffusion coefficient, D_a :

$$D_a = \frac{D_i}{\alpha'} = \frac{D_p n_e}{\alpha'} = \frac{D n_e \delta}{\tau^2 \alpha'} \quad (2.38)$$

where α' = capacity factor or ratio of the moles per unit volume of water-saturated solid, C_s , to the moles per unit volume of liquid, C_l .

The capacity factor is related to the K_d by the equation

$$\alpha' = n_e + \rho_b K_d \quad (2.39)$$

where ρ_b = dry bulk density of the porous media.

Also note that α'/n_e is the familiar retardation factor used in transport modeling:

$$\frac{\alpha'}{n_e} = R_f = 1 + \frac{\rho_b K_d}{n_e} \quad (2.40)$$

It should be noted that these simple relationships are strictly only valid for reversible, linear adsorption reactions with fast kinetics. This point is often overlooked and should not be. Nevertheless, such simplifying assumptions allow for some interesting analysis of common laboratory data and experiments.

Equation 2.40 has been incorporated into the transport equation:

$$\frac{\partial C}{\partial t} = \frac{D}{R_f} \frac{\partial^2 C}{\partial x^2} \quad (2.41)$$

where R_f = retardation factor, as defined in Equations 2.23 or 2.24
 t = time.

Note that Equation 2.41, which is strictly for transport by diffusion, is similar to Equation 2.25, which describes contaminant migration due to advective flow.

Therefore, the apparent diffusion coefficients, D_a , for reactive constituents account for the chemical retardation as well as the physical hindrance to contaminant mobility caused by the small pore sizes and tortuosity of the soil.

2.7 Subsurface Mobile Colloids

2.7.1 Concept of 3-Phase Solute Transport

Contaminant transport models generally treat the subsurface environment as a 2-phase system in which contaminants are distributed between a mobile aqueous phase and an immobile solid phase (*e.g.*, soil). Contaminants with a high affinity for sorbing to rock or vadose zone soils are assumed to be retarded relative to the rate of groundwater flow. However, an increasing body of evidence indicates that under some subsurface conditions, components of the solid phase may exist as colloids¹ that may be transported with the flowing water. Association of contaminants with this additional mobile phase may enhance not only the amount of contaminant that is transported, but also the rate of contaminant transport. Most current approaches to predicting contaminant transport ignore this mechanism not because it is obscure or because the mathematical algorithms have not been developed (Corapcioglu and Kim, 1995; Mills *et al.*, 1991), but because little information is available on the occurrence, the mineralogical properties, the physicochemical properties, or the conditions conducive to the generation of mobile colloids.

There are 2 primary problems associated with studying colloid-facilitated transport of contaminants under natural conditions. First, it is difficult to collect colloids from the subsurface in a manner which minimizes or eliminates sampling artifacts. Sampling artifacts can arise when groundwater is pumped too rapidly, yielding particles that would otherwise remain immobile in the aquifer (Backhus *et al.*, 1993; McCarthy and Degueldre, 1993; Powell and Puls, 1993).

¹ A colloid is any fine-grained material, sometimes limited to the particle-size range of <0.00024 mm (*i.e.*, smaller than clay size), that can be easily suspended (Bates and Jackson, 1979). In its original sense, the definition of a colloid included any fine-grained material that does not occur in crystalline form. The geochemistry of colloid systems is discussed in detail in sources such as Yariv and Cross (1979) and the references therein.

Colloids may also be generated during sampling by exposing groundwater containing readily oxidizable metals, such as Fe(II), to atmospheric conditions and causing the precipitation of fine grain-sized hydrous oxide colloids (Backhus *et al.*, 1993; McCarthy and Degueldre, 1993; Ryan and Gschwend, 1990). Secondly, it is difficult to unambiguously delineate between the contaminants in the mobile-aqueous and mobile-solid phases (Buffle *et al.*, 1992; Degueldre *et al.*, 1989; McCarthy and Degueldre, 1993; Puls, 1990). Using ultrafiltration techniques to accomplish this goal is not entirely satisfactory because it provides only indirect evidence, is subject to a number of artifacts, and usually requires high analytical precision at very low contaminant concentrations (Buffle *et al.*, 1992; Danielsson, 1982; Degueldre *et al.*, 1989; McCarthy and Degueldre, 1993).

2.7.2 Sources of Groundwater Mobile Colloids

Subsurface mobile colloids originate from (1) the dispersion of surface or subsurface soils, (2) decementation of secondary mineral phases, and (3) homogeneous precipitation of groundwater constituents (McCarthy and Degueldre, 1993). First, colloidal particles can be dispersed and become mobile in aquifers as a result of changes in the groundwater chemistry, such as a decrease in ionic strength or changes in ionic composition from a calcium- to a sodium-dominated chemistry. The effect of sodium and ionic strength on colloid suspension stability is interactive such that the dispersive quality of sodium is enhanced at low salt levels (Kaplan *et al.*, 1996).

Geochemical or microbiological changes that result in dissolution of cementing phases, such as iron oxides and calcium carbonate can result in release of colloids. For example, Gschwend *et al.* (1990) observed 10 to 100 mg/l of silica colloids in groundwater receiving recharge from evaporation ponds and a fly ash basin. The infiltrate was enriched in carbon dioxide that dissolved the soil-cementing carbonate mineral, thus releasing the silica colloids. The third source of groundwater mobile colloids is homogeneous precipitation. Changes in groundwater geochemical conditions such as pH, major element composition, redox potential, or partial pressures of CO₂ can induce supersaturation and coprecipitation of colloidal particles. The precipitates can include major elements such as oxides of iron and manganese, calcium carbonates, and iron sulfides, as well as minor elements such as carbonates and sulfides of metals and radionuclides. Mobile colloid precipitates may form when soluble contaminants are introduced into a system resulting in their exceeding the solubility product. For example, Gschwend and Reynolds (1987) observed precipitation of ferrous phosphate colloids (1 to 10 mg/l of 100 nm-sized particles) down gradient of a sewage infiltration site. Solubility calculations suggested that the dissolved phosphate ions from the sewage and reduced iron in the aquifer exceeded the solubility product of ferrous phosphate, resulting in the formation of insoluble colloids. Other studies have documented the formation of iron oxide colloids in groundwater as a result of changes in pH and oxygenation that caused the solubility limit of Fe(III) oxides to be exceeded (Liang *et al.*, 1993). Many strongly hydrolyzing radionuclides also form submicron-sized particles. Increases in solution pH have been shown to induce the formation of plutonium-, uranium-, and americium-oxide colloids in carbonate systems (Ho and Miller, 1986; Kim, 1986).

2.7.3 Case Studies of Mobile-Colloid Enhanced Transport of Metals and Radionuclides

Although the concept of colloid-facilitated transport is often invoked to account for anomalies between predicted and observed transport of contaminants, little field or experimental verification of this potentially important phenomenon is available (McCarthy and Degueldre, 1993). There have been a few field studies describing colloid-facilitated transport and these studies have provided only circumstantial evidence that this is in fact the actual mechanism responsible for the enhanced transport of contaminants (Buddemeier and Hunt, 1988; Degueldre *et al.*, 1989; Kaplan *et al.*, 1994a; Kaplan *et al.*, 1995a; Penrose *et al.*, 1990).

Although laboratory studies at Los Alamos National Laboratory (LANL) predicted that the movement of actinides in subsurface environments would be limited to less than a few meters, both americium and plutonium were detectable in monitoring wells as far as 3,390 m down gradient from the point source (Penrose *et al.*, 1990). Almost all of the americium and plutonium in the groundwater at the 3,390 m well were associated with colloids 0.025 to 0.45 μm in diameter. Similarly, based on laboratory measurements using site-specific soils and a 2-phase solute transport code, americium, curium, plutonium, and uranium were expected to travel less than 10 m in the F-Area of the Savannah River Site; the contaminants were found associated with groundwater colloids 1,200 m away from the point source (Kaplan *et al.*, 1994a). To a lesser extent, chromium, copper, nickel, and lead were also detected directly on suspended groundwater particles collected from the F-Area study site (Kaplan, 1994b, 1995a). The reader is cautioned that, because most transport predictions do not account for preferred flow paths, the interpretation that colloid-facilitated migration is the best explanation for such enhanced migration is still being debated.

2.8 Anion Exclusion

Dissolved chloride, bromide, and nitrate are usually reported to travel through natural systems or soil columns at the same rate as, or faster than, water (James and Rubin, 1986; McMahon and Thomas, 1974). Anion exclusion, the mechanism by which anions move faster than water, occurs when the diffuse double layer, an extension of a particle's negative surface charge into the surrounding solution, repulses anions (Sposito, 1984). By excluding anions from the diffuse double layer, where water is relatively immobile, the system restricts anions to the faster moving pore water, resulting in an average rate of anion transport that is greater than the average pore water velocity defined by Darcy's Law (James and Rubin, 1986; McMahon and Thomas, 1974). Anion exclusion is more pronounced with higher cation exchange capacity (*i.e.*, negative charge) of the soil or rock. For example, smectites ($\text{CEC} \approx 3 \text{ meq/g}$) exhibit anion exclusion to a greater degree than do the kaolinite ($\text{CEC} \approx 0.2 \text{ meq/g}$) minerals (McMahon and Thomas, 1974).

The implication of anion exclusion for anionic contaminants (*e.g.*, nitrates, chloride, chromate, pertechnetate) and anionic complexes [*e.g.*, $\text{UO}_2(\text{CO}_3)_2^{2-}$] is that they may be able to travel through the subsurface at a rate greater than water. There is some indirect evidence that anion exclusion may exist for pertechnetate. In an unsaturated column study, pertechnetate breakthrough (C/C_0 , 0.5) occurred at 0.95 pore volumes, whereas for tritium, a conservative

tracer, breakthrough occurred at 1.02 pore volumes; that is, pertechnetate may have traveled 5 percent faster than tritium (Gee and Campbell, 1980). Chloride breakthrough in these columns occurred at 0.80 pore volumes, or 22 percent faster than tritium, providing evidence that the transport of chloride may be affected by anion exclusion.

2.9 Summary

The objective of this chapter is to present a primer on the key geochemical processes affecting contaminant transport in subsurface environments. References to important review articles and books are included for each of the major subject areas: aqueous geochemical processes, sorption, diffusion, subsurface mobile colloids, and anion exclusion. These processes are summarized in Table 2.5.

Particular attention is directed at describing the geochemical processes affecting chemical retardation. A brief discussion of mechanistic and semi-empirical adsorption models. Incorporating mechanistic and semi-mechanistic adsorption concepts into transport models is desirable because the models become more robust and scientifically defensible. However, mechanistic models are rarely, if ever, applied to field-scale problems. The reasons for this are the following: (1) mechanistic models require a more intense data collection effort than will likely be available to the majority of transport modelers, licensee requestors, or responsible parties; (2) installing these mechanistic adsorption models into existing transport codes is quite complex; and (3) mechanistic adsorption models require full characterization of the mineral surfaces, information that is impossible to obtain in natural heterogeneous soils. Importantly, these models provide a paradigm for using simpler models, such as the conditional K_d model.

Conditional K_d values can be derived from laboratory or field experiments. Unlike the thermodynamic K_d term, they are less rigorously defined in that the conditional K_d values are not necessarily limited to a single aqueous species and single solid phase. This broader definition lends itself more readily to natural systems, while at the same time resulting in several technical issues and complexities. The understanding of the important geochemical factors affecting the transport of the contaminants of interest is critical for site-specific calculations.

Table 2.5. Summary of chemical processes affecting attenuation and mobility of contaminants.

Process	Mechanism	Enhancement of Attenuation or Mobility of Contaminant?	Key Facts
Aqueous Complexation	Reaction where an aqueous molecular unit (ion) acts as a central group to attract and form a close association with other atoms or molecules	May enhance attenuation or mobility, depending on contaminant and geochemical conditions	<ul style="list-style-type: none"> • Function of pH and redox • Complexation may lower the potential for adsorption and/or increase solubility, both of which can enhance potential for mobility • Complexes may more readily bond to soils and thus retard migration • Organic ligands from humic materials can be present in significant concentrations and dominate contaminant complexation in some systems
Redox Reactions	Reaction where electrons are transferred completely from one species to another	May enhance attenuation or mobility, depending on contaminant and geochemical conditions	<ul style="list-style-type: none"> • Change in redox status changes aqueous speciation which may increase or decrease adsorption and solubility • If redox status is sufficiently low to induce precipitation of sulfide minerals, - reprecipitation of some contaminants may be expected • More difficult to predict mobility of redox-sensitive species because many redox reactions are kinetically slow in natural groundwater, and several elements may never reach equilibrium between their various valence states

Table 2.5. Continued.

Process	Mechanism	Enhancement of Attenuation or Mobility of Contaminant?	Key Facts
Adsorption and Ion Exchange	Special case of a complexation reaction where there is a net accumulation of a contaminant at the interface between a solid phase and an aqueous-solution phase; does not include the development of a 3-dimensional molecular structure	Enhances Attenuation	<ul style="list-style-type: none"> • Occurs primarily in response to electrostatic attraction • Very dependent on pH and mineralogy • Anion adsorption is greatest at low pH and decreases with increasing pH • Cation adsorption is greatest at high pH and decreases with decreasing pH. • Some contaminants may be present as cations or anions depending pH • Totally-to-partially reversible; decline in contaminant concentration in groundwater may result in desorption and release of adsorbed contaminant to groundwater • Likely key process controlling contaminant mobility in areas where chemical equilibrium exists

Precipitation	Special case of a complexation reaction in which the complex formed by 2 or more aqueous species is a solid with 3-dimensional molecular structure	Enhances Attenuation	<ul style="list-style-type: none"> • Very dependent on pH and redox • Totally-to-partially reversible; decline in contaminant concentration in groundwater may result in dissolution of precipitated contaminant to groundwater • Likely process where chemical nonequilibrium exists, an area where high contaminant concentrations exist, or where steep pH and/or redox gradients exist
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Table 2.5. Continued.

Process	Mechanism	Enhancement of Attenuation or Mobility of Contaminant?	Key Facts
Diffusion	Molecular process of transport of matter in the absence of bulk flow	Enhances Mobility	<ul style="list-style-type: none"> • Flux of matter due to diffusion is proportional to concentration gradient
Subsurface Colloids	Contaminants associated with suspended fine-grained material (smaller than clay size) that may be transported with flowing groundwater	Enhances Mobility	<ul style="list-style-type: none"> • Little information on occurrence, mineralogical and physicochemical properties, or conditions conducive to the generation of mobile colloids • May originate from the dispersion of soils, decementation of secondary mineral phases, and/or precipitation of groundwater constituents • Difficult to collect colloids from subsurface in a manner that minimizes or eliminates sampling artifacts • Difficult to unambiguously delineate between the contaminants in the mobile-aqueous and mobile-solid phases

Anion Exclusion	Occurs when the diffuse double layer, an extension of a particle's negative surface charge into the surrounding solution, repulses anions	Enhances Mobility	<ul style="list-style-type: none"> • By excluding anions from the diffuse double layer, where water is relatively immobile, anions restricted to the faster moving pore water, resulting in an average rate of anion transport greater than the average pore water velocity defined by Darcy's Law • more pronounced with higher cation exchange capacity (<i>i.e.</i>, negative charge) of the soil or rock
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